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Bis-cyclometallated Ir(III) complexes containing 2-(1*H*-pyrazol-3-yl)pyridine ligands; influence of substituents and cyclometallating ligands on response to changes in pH†

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Bis-cyclometallated Ir(III) complexes containing 2-(1*H*-pyrazol-3-yl)pyridine ligands have been synthesised. Their absorption is almost unchanged with changes in pH however the emission intensities vary by a factor of up to three and the complexes have emission pK_as in the range 8.0 to 10.0. Substituents on the pyrazole have only a minor effect on the emission pK_a. Surprisingly the complexes with phenylpyrazole cyclometallated ligands **3aL$_{1-3}$** showed an intensity decrease with increasing pH (switch off) whilst the corresponding phenylpyridine ones **3cL$_{1-3}$** showed an increase in emission intensity with increasing pH. Putting electron-withdrawing CF_3 substituents on the cyclometallating phenyls reduced the pK_a of the complexes to 6.8–7.8, thereby extending the useful pK_a range; however, in general it tended to reduce the magnitude of the change in emission intensity. Surprisingly the CF_3-substituted complexes also showed a complete reversal in the direction of the intensity change when compared to their respective unsubstituted congeners.

Introduction

Luminescent pH sensors have attracted significant interest for measuring pH in biological environments due to their excellent sensitivity, minimal damage to living samples, specificity, the availability of a wide range of indicator dyes, high signal-to-noise ratios and the ability to continuously monitor rapid pH changes. Furthermore, fluorescence microscopic imaging allows mapping of the spatial and temporal distribution of H^+ within living cells.[1] To date, pH sensors have primarily focussed on organic molecules; however, transition metal and rare earth metal complexes have also been studied.[2] Transition metal complexes are attractive as possible pH sensors due to significant Stokes shifts for easy separation of excitation and emission, tuneable emission wavelength, and relatively long emission lifetimes compared to organic molecules allowing for possible luminescent lifetime imaging of pH.[3] Several luminescent complexes of the platinum group metal ions have been used as pH sensors, notably Ru(II),[4] Re(I),[5] and Pt(II).[1a,6]

Iridium complexes have also been used for pH sensing. An early example by Licini and Williams used Ir bis-terpyridine complexes, (Fig. 1) containing either pyridyl or phenol substituents as the pH responsive groups which exhibit changes in lifetime and intensity with changing pH.[7] The pK_as of the complexes ranged from 4.1 (*cf.*, pyridinium pK_a = 5.25) to 8.1 (*cf.*, phenol pK_a = 10.0), in both cases the cationic electron-withdrawing metal terpyridyl unit reduces the basicity of the pendant group, pyridine or phenol, respectively.

The coordination of a functionalised ligand to a metal tends to lead to a reduction in electron density due to electron donation to the metal and hence should lead to a lowering of the pK_a for the ligand in the ground state. However, it should

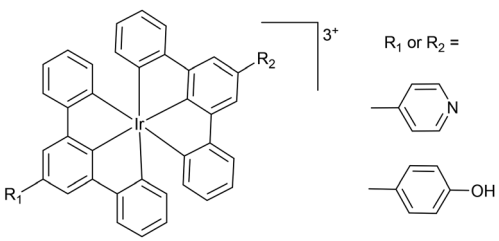

Fig. 1 Early examples of pH sensitive luminescent Ir(III) complexes.[7]

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†Electronic supplementary information (ESI) available: Crystallographic data (CIF), extra molecular structures, absorption and emission spectra and pH titrations, NMR spectra. CCDC 2014697–2014704. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0dt02434a

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be noted that it is harder to predict the outcome for an excited state.

In the last 20 years there has been huge interest in the use of cyclometallated Ir(III) complexes of general formula $[Ir(C^N)_2(X^Y)]^{n+}$ (C^N = a cyclometallated ligand, X^Y = a neutral or anionic bidentate ligand n = 0,1; Fig. 2 structure **A**) which have interesting photophysical properties and have found applications particularly in OLEDS, sensors and as labels for biological imaging.[8] A comparatively small number show pH responsive emission, changing wavelength and/or intensity of emission. A number of different pH responsive ligands have been used, and some of these are shown in Fig. 2. The pH responsive group can be on the cyclometallating (C^N) ligands or on the ancillary (X^Y) ligand. For example, tris-cyclometallated complexes with protonatable pyridyl[9] or amine[10] substituents (**B** or **C** Fig. 2) have been reported. Bis-cyclometallated complexes with ligands **D** were non-emissive at low pH 2–5 but gave red emission at higher pH which was ascribed to deprotonation of the carboxylic acid groups.[11] The pK_a value was approximately 7.0, suggesting that the probe may useful for monitoring pH in biological systems.

Several proton responsive N^N ligands have been used as the ancillary X^Y ligand in bis-cyclometallated complexes (Fig. 2 **E–H**). For example, functionalised bipyridine ligands, with morpholine **E**[12] or carboxylic acid substituents **F**.[13] Several groups have investigated complexes with imidazole or benzimidazole containing ligands *e.g.* **G**.[14] Similar carboline-containing ligands **H** gave pH-sensitive iridium(III) complexes used in lysosome targeted photodynamic therapy (PDT).[15] The complexes were more emissive at low pH with pK_a values between 3.6 and 4.4.

Although, imidazole-based ligands have been investigated, pyrazole ligands with an NH moiety have been much less studied. Lam *et al.* studied a Re-carbonyl complex containing a bidentate pyrazolyl–pyridine.[5b] Cyclometallated Pt complexes with tridentate pyrazolyl-containing ligands have also been studied which show pH dependent emission some of which have been in used in cell imaging.[6b,16] Hence, we have investigated Ir(III) bis-cyclometallated complexes with 2-(1*H*-pyrazol-3-yl)pyridine ligands. 2-(1*H*-pyrazol-3-yl)pyridine itself has a pK_a of 11.6.[17] We have investigated the effect of the nature of the cyclometallated ligands, phenylpyrazole and phenylpyridine respectively and ones with an electron-withdrawing CF_3 substituent, and of substituents on the pyrazole.

Results and discussion

Synthesis

The bis-cyclometallated dimers **1a–d** (Chart 1) were prepared by a literature method[18] and the data are consistent with those published.[18,19] The syntheses of cationic complexes **2aHL$_{1-3}$** are outlined in Scheme 1. The dimer **1a** was reacted with the relevant 2-(1*H*-pyrazol-3-yl)pyridine (**HL$_{1-3}$**) in the presence of KPF_6 in methanol at 60 °C under microwave irradiation for 20–40 minutes (see Experimental section). After work up, complexes **2aHL$_{1-3}$** were formed in good to excellent yields.

^{1}H and ^{13}C NMR spectra for all the complexes were assigned using two-dimensional NMR experiments such as TOCSY, COSY, NOESY, and HMQC. The coordination of the N^N ligand removes the C_2-symmetry of the dimers, causing the two C^N ligands to become inequivalent and therefore doubling the number of peaks for the cyclometallated ligands. The ^{1}H and ^{13}C NMR spectra of **2aHL$_{1-3}$** are similar to each other therefore, only the assignment of complex **2aHL$_1$** is discussed in detail.

The ^{1}H NMR spectrum of complex **2aHL$_1$** contains twenty-one aromatic environments. There are two doublets of doub-

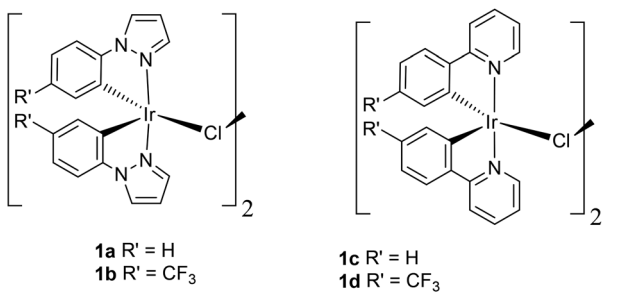


Chart 1 Iridium dimers used.

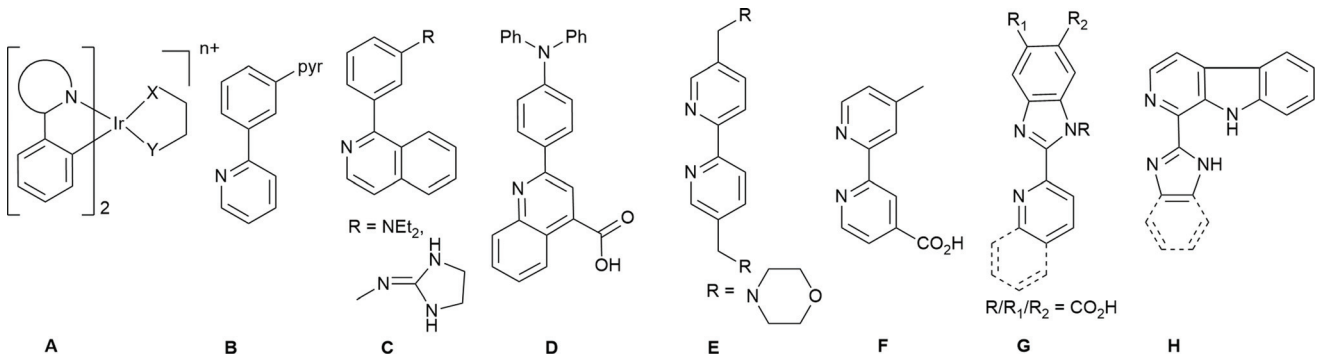
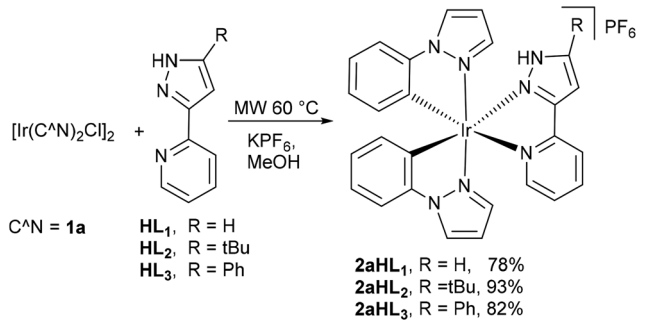
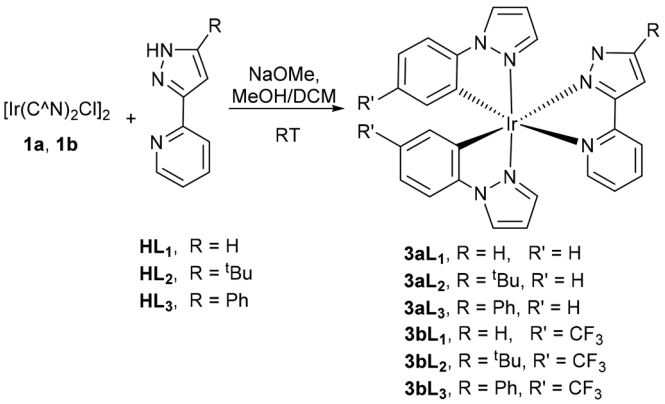


Fig. 2 Examples of pH responsive cyclometallating ligands (**B** to **D**) or ancillary ligands ligands (**E** to **H**) used in bis- or tris-cyclometallated Ir complexes.



Scheme 1 Preparation of cationic bis-cyclometallated phenylpyrazole complexes.



Scheme 2 Preparation of neutral bis-cyclometallated complexes of phenyl pyrazole.

lets at δ 6.30 and 6.32, characteristic of cyclometallated phenyl protons which are shifted to high field due to ring current effects.[20] This then allows assignment of the signals for the phenyl and pyrazole rings of the C^N ligands using the TOCSY and NOESY spectra (Fig. S1 and 2†). Likewise, the protons of the pyrazole of the N^N ligand are easily identified in the TOCSY spectrum as doublets at δ 7.83 and δ 7.20 slightly shifted downfield compared to the free ligand (by *ca.* δ 0.4 and 0.2, respectively) presumably due to the coordination of the (N^N) ligand to the metal. The doublet at δ 7.20 shows an NOE to a doublet of triplets at *ca.* δ 8.20 which is therefore assigned as the closest pyridine proton (H_e see ESI† for NMR labelling) and the other pyridine protons H_{f-h} are assigned from the TOCSY and COSY spectra. The protons H_{e-g} are shifted slightly downfield compared to the free ligand (*ca.* δ 0.2 to 0.4) as might be expected on coordination to the metal, however, the proton next to the N atom (H_h) is observed at δ 8.01 about δ 0.7 upfield compared to the free ligand (δ 8.68) due to ring currents from the neighbouring phenyl ring (A), as noted previously, *e.g.* for $[Ir(R\text{-}ppz)_2(bipy)]PF_6$.[18] Proton H_h also shows an NOE to a pyrazole proton multiplet at *ca.* δ 7.07 which is therefore assigned as H_{7B}. This distinguishes the two cyclometallating ligands and hence allows for assignment of all the other protons. The NH proton was not observed, probably due to exchange with D_2O in the solvent (CD_3CN). The ^{13}C NMR spectrum showed the expected number of signals, and were assigned using the HSQC and HMBC spectra. The high resolution mass spectrum (ASAP) shows a molecular ion with characteristic Ir isotopes pattern for the cation at *m*/*z* 624.1497 (624.1488 calculated for $C_{26}H_{21}{}^{193}IrN_7$).

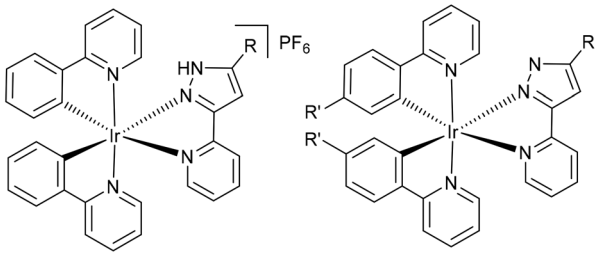
The ^1H NMR spectra of **2aHL$_2$** and **2aHL$_3$** are similar to that of **2aHL$_1$** except for the substituent on the N^N pyrazole, a singlet due to a ^{t}Bu at δ 1.26 for **2aHL$_2$** and extra signals in the aromatic region for **2aHL$_3$**. For **2aHL$_3$** a downfield singlet at δ 12.01 was assigned to the NH proton. The ^{13}C NMR spectra showed the expected number of signals and both complexes showed an ion corresponding to the cationic complex in their high resolution (ASAP) mass spectra.

The neutral complexes **3aL$_{1-3}$** corresponding to loss of a proton from **2aHL$_{1-3}$** were synthesised in good yields by reaction of dimer **1a** with ligands **HL$_1$**–**HL$_3$** and NaOMe in a mixture of DCM/methanol (2 : 1) (Scheme 2). Additionally, a CF_3 substituted dimer **1b** was also used to investigate the effect of an electron withdrawing substituent on the cyclometallating ligand, providing complexes **3bL$_{1-3}$**.

The ^1H and ^{13}C NMR spectra of **3aL$_{1-3}$**, are similar to those for **2aHL$_{1-3}$**, respectively, and assignments have been made on this basis. As expected, in the majority of cases the deprotonation of the ancillary ligand causes an upfield shift of the protons of the N^N ligand in the ^1H NMR spectra compared to their corresponding cationic complexes. For example, for **3aL$_1$** the pyrazole protons $H_{a,b}$ are observed as mutually coupled doublets at δ 7.47 and 6.82, respectively, upfield compared to the corresponding signals in the cationic complex **2aHL$_1$** (δ 7.83 and 7.20 respectively) consistent with deprotonation of the pyrazole. Unusually, for **3aL$_1$** the most upfield resonance in the aromatic region is a pyrazole proton not a cyclometallated phenyl. The spectra of the CF_3-substituted complexes **3bL$_{1-3}$** are similar to those of the unsubstituted complex but with two fewer resonances in the aromatic region. The ^{19}F NMR spectra of **3bL$_{1-3}$** exhibit two singlets at about −60 ppm corresponding to two different CF_3 groups. All of the neutral complexes show ions due to $[M + H]^+$ in their high-resolution mass spectra.

The corresponding complexes containing cyclometallated phenylpyridine ligands in place of phenylpyrazole were prepared by analogous procedures to give cationic complexes **2cHL$_{1-3}$** and neutral complexes **3cL$_{1-3}$** and CF_3-substituted complex **3dL$_2$** respectively (see Chart 2). These were fully characterised by ^1H and ^{13}C NMR spectroscopy and high-resolution mass spectra.

The ^1H NMR spectra of **2cHL$_{1-3}$** show the cyclometallated phenyl protons as the most upfield aromatic signals, between δ 6.23, and 6.35. The pyridine proton next to nitrogen for both the cyclometallating ligands and the N^N ligand are all influenced by ring currents from the other ligands and hence are shifted upfield compared to the free ligands, being observed between δ 7.9 and 7.5. The ^1H NMR spectra for neutral complexes **3cL$_{1-3}$** show the cyclometallated phenyl protons between δ 6.23 and 6.39 within 0.1 ppm of the related cationic



2cHL$_1$, R = H, R' = H
2cHL$_2$, R = ^{t}Bu, R' = H
2cHL$_3$, R = Ph, R' = H

3cL$_1$, R = H, R' = H
3cL$_2$, R = ^{t}Bu, R' = H
3cL$_3$, R = Ph, R' = H
3dL$_2$, R = ^{t}Bu, R' = CF_3

Chart 2 Labelling of bis-cyclometallated complexes of phenylpyridine.

complexes. As for **3aL$_{1-3}$** deprotonation of the pyrazole NH proton **3cL$_{1-3}$** leads to an approximately 0.5 ppm upfield shift for pyrazole proton H_b. All the other protons are within 0.2–0.3 ppm of the signals in the corresponding cationic complexes **2cHL$_{1-3}$**. The ^{13}C NMR spectra show the expected number of signals for **2cHL$_{1-3}$**. The ^{1}H and ^{13}C NMR spectra of **3dL$_2$** are similar to **3cL$_2$**, except the signals for one proton on each the phenyl rings of the C^N ligands have been replaced by a CF_3 group, as confirmed by ^{19}F NMR spectroscopy. The high-resolution mass spectra (ASAP) each show a molecular ion for the cations **2cHL$_{1-3}$** and the protonated molecular ions for **3cL$_{1-3}$** and **3dL$_{1-3}$**.

X-ray crystallography

The cationic complexes were relatively easy to crystallise as their PF_6 salts, hence complexes **2aHL$_{1-3}$** and **2cHL$_{1-3}$** were characterised by X-ray crystallography. In addition, two of the neutral molecules **3aL$_2$** and **3cL$_3$** were also characterised by X-ray crystallography. As examples the structures of two cationic/neutral pairs **2aHL$_2$** and **3aL$_2$**, and **2cHL$_3$** and **3cL$_3$** are shown in Fig. 3 and 4 respectively, the remaining structures are in Fig. S3 and S4† with selected bond lengths and angles in Tables S1 and S2.†

All the crystal structures show the expected distorted octahedral coordination geometry with *cis* metallated carbons and *trans* nitrogen atoms. The chelate bite angles for the cyclometallated ligands are all about 80°, and about 75° for the N^N

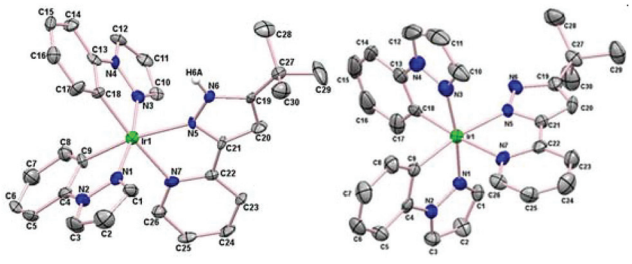


Fig. 3 Left, structure of the cation of **2aHL$_2$** and right the structure of **3aL$_2$** showing 50% ellipsoids. All hydrogen atoms (except NH) have been omitted for clarity.

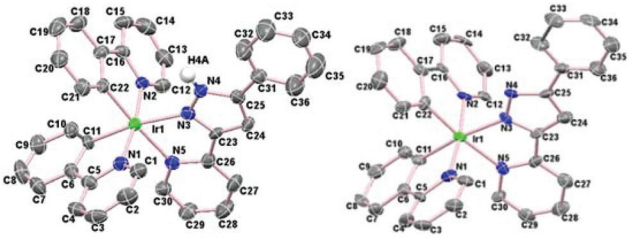


Fig. 4 Left, structure of the cation of **2cHL$_3$** and right the structure of **3cL$_3$** showing 50% ellipsoids. All hydrogen atoms (except NH) have been omitted for clarity.

ligands. The Ir–N bond lengths to the N^N ligand are longer than those to the cyclometallating ligands, due to the former being *trans* to the C atoms, as observed previously.[21] For example, for complex **2aHL$_1$**, [Ir(1)–N(5), 2.116(7) and Ir(1)–N(7), 2.148(6) Å] are longer than [Ir(1)–N(1), 2.036(7), and Ir(1)–N(3), 2.031(6) Å] similar trends are seen for complexes **2aHL$_{2-3}$**. The same trend in Ir–N bond lengths is also seen for the neutral complexes. The Ir–N bond distance to the anionic pyrazole of the N^N ligand [2.122(6) Å in **3aL$_2$** and 2.088(7) Å in **3cL$_3$**] is shorter than that in the cationic analogue [2.175(8) Å in **2aHL$_2$**, and 2.149(4) Å in **3cL$_3$**] though the other Ir–N and Ir–C bonds and the chelate bite angles are statistically almost the same in both pairs of complexes. The structures of **2aHL$_{1-3}$** and **2cHL$_1$** and **2cHL$_3$** show the presence of waters of crystallisation and most of the structures show hydrogen bonding from the NH of the protonated pyrazole to the PF_6 anion or to a water molecule.

Photophysical properties

The UV-vis absorption spectra of all 16 complexes are shown in Fig. S5–S8† and the data are collated in Table S3.† Cationic complexes **2aHL$_{1-3}$**, and their neutral counterparts **3aL$_{1-3}$** are shown in Fig. S5† whilst the CF_3-substituted complexes **3bL$_{1-3}$** are compared with their unsubstituted analogues, **3aL$_{1-3}$** in Fig. S6.† Similarly, spectra for phenylpyridine complexes **2cHL$_{1-3}$**, and **3cL$_{1-3}$** are in Fig. S7† and **3cL$_2$**, is compared with **3dL$_2$** in Fig. S8.† All the complexes show strong bands between 225 and 300 nm due to $\pi \rightarrow \pi^*$ transitions in addition the phenylpyridine complexes **2cHL$_{1-3}$**, **3cL$_{1-3}$** and **3dL$_2$** show weak bands between 380–405 nm (possibly having contributions from ^{1}MLCT transitions). Adding a CF_3 substituent to the C^N ligand causes only minor changes, and these are in the short wavelength region. The substituent on the N^N ligand also has very little effect on the λ_{max}. For both the phenylpyrazole and phenylpyridine complexes there are only minor differences in uv-vis spectra between the cationic and neutral species and these are in the uv region, a slight red shift (10 to 30 nm) in λ_{max} occurring on deprotonation. Since there is no significant change (<20%) in absorbance at any wavelength, these complexes would not be expected to be good pH sensors in their ground states.

Emission spectra of the complexes were run in MeCN in aerated solutions. Each pair of cationic and neutral complexes

(*e.g.*, **2aHL$_1$** and **3aL$_1$**) were irradiated at the same excitation wavelength (see Fig. S9 and 10† for excitation spectra). The emission spectra of phenylpyrazole cationic complexes **2aHL$_{1-3}$** and their neutral analogues **3aL$_{1-3}$** are shown in Fig. 5a whilst those of **3aL$_{1-3}$** are compared with their CF_3-substituted analogues **3bL$_{1-3}$** in Fig. 5b and all the associated data are reported in Table S4.†

All three cationic complexes **2aHL$_{1-3}$** show a broad emission band, each with a similar λ_{max} at 502, 495, and 508 nm, respectively. Hence, the substituent on the pyrazole has only a small effect on the emission wavelength. The corresponding neutral complexes **3aL$_{1-3}$** show similar spectra with a slight blue shift in λ_{max} of 27 nm (1053 cm^{-1}) for **3aL$_1$**, 2 nm (82 cm^{-1}) for **3aL$_2$** and 12 nm (476 cm^{-1}) for **3aL$_3$**. The emission intensity for the neutral complexes **3aL$_{1-3}$** are all reduced by about 50% compared with the cationic complexes **2aHL$_{1-3}$**. Hence, these complexes have potential as luminescent pH sensors. Neutral complexes **3bL$_{1-3}$** with an electron-withdrawing substituent (CF_3) on the phenyl ring each show a broad emission band which is blue-shifted compared to the corresponding unsubstituted complexes **3aL$_{1-3}$**, with **3bL$_2$** showing the largest shift of 35 nm (1550 cm^{-1}) (Fig. 5b and Table S4†), respectively. A blue shift in emission by addition of electron-withdrawing groups to the C^N cyclometallating ligands is a well-known phenomenon that has been ascribed to the electron-withdrawing group stabilising the HOMO.[18,22]

The emission spectra of the corresponding phenylpyridine complexes **2cHL$_{1-3}$**, and **3cL$_{1-3}$** are shown in Fig. 6 and their data are reported in Table S4.† Complex **2cHL$_1$** shows a broad emission band (λ_{max} 505 nm); however, complexes **2cHL$_{2-3}$** both show some structure in the emission band. As for the phenylpyrazole complexes, changing the **R$_2$** group on the N^N ligand has only a small effect on the emission wavelength. The neutral complexes **3cL$_{1-3}$** show similar spectra to the cationic complexes, with a broad emission band with shoulders. Surprisingly there is no significant change in emission intensity between the cationic and neutral complexes, though the neutral complexes are slightly more emissive than the cationic ones which is the opposite case to the phenylpyrazole complexes. Hence, these are not expected to be good pH sensors in their excited states (see pH titrations below for further discussion). The neutral CF_3-substituted complex **3dL$_2$** showed a λ_{max} at 502 nm, a small blue shift (*ca.* 4 nm) compared to the corresponding unsubstituted complex **3cL$_2$**, and also shows a distinct shoulder at longer wavelength *ca.* 533 nm (Fig. S10†).

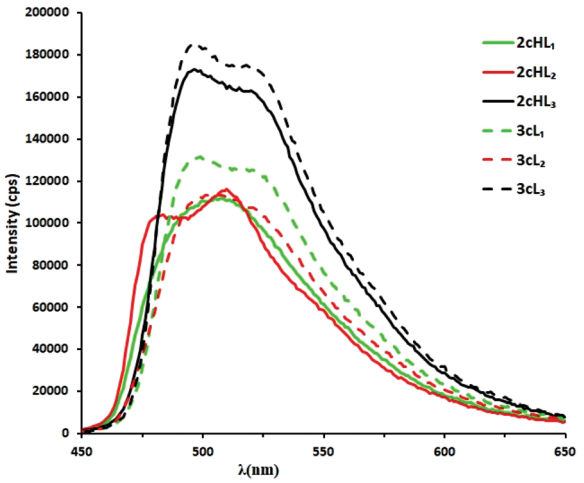


Fig. 6 Emission spectra of cationic and neutral complexes **2cHL$_{1-3}$** (—) and **3cL$_{1-3}$** (– – –), in MeCN at 0.02 mM at room temperature in air; excitation at 320–325 nm.

In conclusion, the UV-vis absorption spectra of all the complexes show strong bands between 200 and 300 nm due to $\pi \rightarrow \pi^*$ transitions, with the phenylpyridine complexes also showing weak bands between 380–405 nm. All the complexes are emissive at room temperature in solution in air. There is no significant variation in emission wavelength upon changing the substituent on the ancillary N^N ligands, and there is very

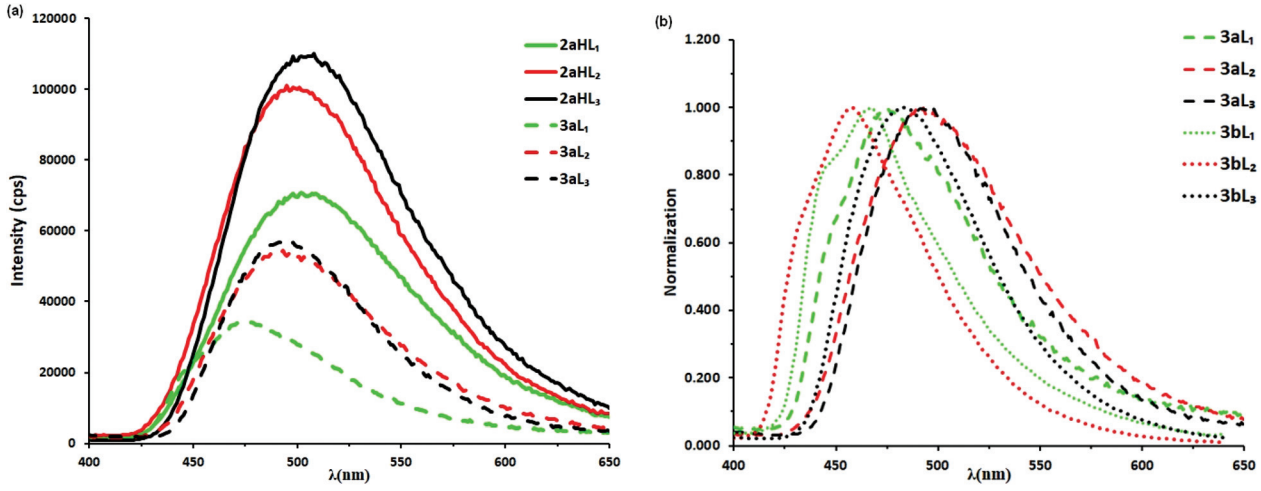


Fig. 5 Emission spectra of (a) cationic and neutral complexes **2aHL$_{1-3}$** (—) and **3aL$_{1-3}$** (– – –), (b) normalised emission spectra of neutral complexes **3aL$_{1-3}$** (– – –) and **3bL$_{1-3}$** (….), all in MeCN at 0.02 mM at room temperature in air; excitation at 320–325 nm.

little change in λ_{max} on deprotonation, except for complex **3aL$_1$** which shows a blue shift of approximately 27 nm. Substituting H with an electron-withdrawing CF_3 group on the C^N ligand causes a blue shift in the emission spectrum, consistent with other bis-cyclometallated Ir complexes.[18,22] The effect of changing the cyclometallated ligand from phenylpyrazole to phenylpyridine is not uniform, giving a red shift in some cases and a blue shift in others. This is further complicated by the presence of shoulders on some bands.

pH titrations

To investigate their potential application as pH sensors, pH titrations of the complexes were carried out in MeCN/H_2O (1 : 9) (see Experimental for details). As expected from the studies of the isolated neutral and cationic complexes there is very little change in the uv-vis spectra with changing pH, hence absorption spectra cannot not be used to determine ground state pK_a values. The emission pK_a values[23] for the complexes were determined by the change in emission intensity with pH over the range *ca.* 3 to 12.5.

As an example, the emission pH titration data and pK_a values of complex **3aL$_1$** are illustrated in Fig. 7. The emission intensity of **3aL$_1$** at 500 nm was relatively unchanged between pH 7.5 and pH 3.7, but above pH 7.5, there was a gradual decrease in emission intensity by about a factor of two to around pH 10, above which the intensity remained essentially constant until pH 12.3. Over the full pH range studied, there is a small blue shift (*ca.* 6 nm) in λ_{max}. The emission pK_a value was determined to be about 9.9 at the equivalent point, which is more acidic than the free 2-(1*H*-pyrazol-3-yl)pyridine ligand itself (pK_a 11.6).[17]

The emission pH titration spectra of complexes **3aL$_{2-3}$** (Fig. S12 and 13†) were similar to that of **3aL$_1$**. In both complexes the emission intensity was relatively constant over the pH range *ca.* 4.9–7.5 but then decreased at higher pH by a factor of *ca.* 2 for **3aL$_2$** and *ca.* 1.3 for **3aL$_3$**. The emission pK_a values of complexes **3aL$_2$** and **3aL$_3$** were determined to be *ca.* 10.0 and 8.9, respectively (Fig. S10 and 11†), which are more acidic than the corresponding free ligands at 12.3 and 11.6, respectively.[17] Hence, all three complexes **3aL$_{1-3}$** can function as pH sensors. However, even though the pK_a of the complexes is between 1.7 and 2.7 units lower than for the free ligands, none of them are low enough to be of use as biological pH sensors. To lower the pK_a further the complexes need to be made more acidic. Hence, complexes **3bL$_{1-3}$** with electron-withdrawing CF_3 groups on the cyclometallating phenyls were examined.

The emission pH titration of complexes **3bL$_{1-3}$** (Fig. S14–16†) did show changes with pH, however, for all three complexes replacing H with the electron-withdrawing CF_3 group on the C^N ligand led to a complete reversal of the shape of the pH titration curve. Thus, at low pH, the complexes show low emission and at high pH the emission intensity is higher, which is the exact opposite of complexes **3aL$_{1-3}$**. From the emission intensity changes, a pK_a value of 6.8 was determined for **3bL$_1$** which is much smaller than the pK_a (9.9) for the unsubstituted complex **3aL$_1$**. The emission **pH** titration spectra of **3bL$_2$** and **3bL$_3$** were similar to that of **3bL$_1$**. Showing a relatively small (1.2–1.3 fold) increase in intensity with increasing pH. The pK_a values of **3bL$_2$** and **3bL$_3$** were calculated to be 7.8 and 7.5, respectively, both lower than the pK_a of the unsubstituted analogues **3aL$_2$** and **3aL$_3$** of 10.0 and 8.9, respectively. Hence, addition of the CF_3 substituents has, as desired, lowered the pK_a of the complexes by between 1.4 and 3.1 units. As noted above, the emission intensity of the CF_3-substituted complexes **3bL$_1$** increases with increasing pH whilst the intensity of the unsubstituted analogues **3aL$_1$** decreases with increasing pH. The reason for this difference is not known. In addition, the complexes, particularly **3bL$_2$** and **3bL$_3$** showed only a small change in emission intensity per unit change in pH and hence will clearly not be particularly good sensors. The

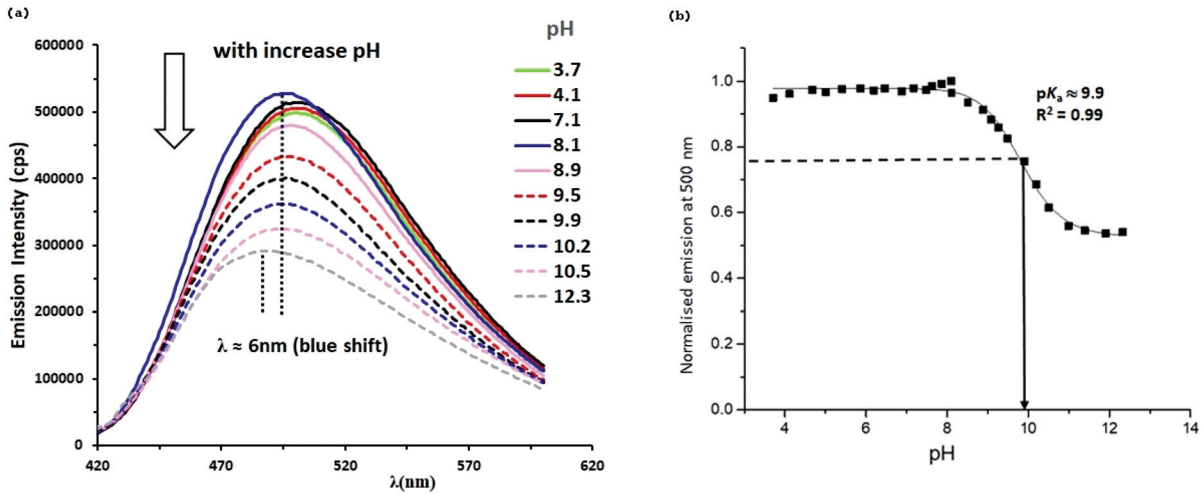


Fig. 7 (a) Selected emission spectra of complex **3aL$_1$** (0.02 mM) at various pH values in MeCN/H_2O (1 : 9), in air with excitation at 324 nm. (b) Plot of normalised emission intensity of complex **3aL$_1$** against pH.

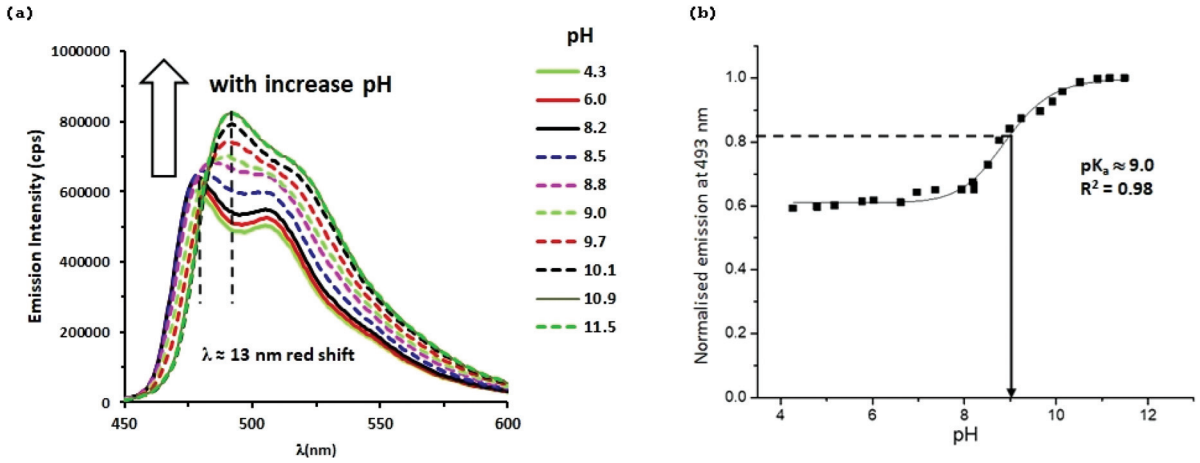


Fig. 8 (a) Selected emission spectra of complex **3cL$_1$** (0.02 mM) at various pH values in MeCN/H_2O (1 : 9), in air with excitation at 324 nm. (b) Plot of normalised emission intensity of complex **3cL$_1$** against pH.

smaller change in intensity could be due to reduced quantum yields or may just be increased triplet character and hence more quenching by oxygen.

As mentioned above the emission spectra for cationic and neutral phenylpyridine complexes **2cHL$_{1-3}$** and **3cL$_{1-3}$** were rather similar however full pH titrations were still carried out. The results for **3cL$_1$** are shown in Fig. 8 and those for **3cL$_{2-3}$** are in Fig. S17 and 18.†

Complex **3cL$_1$** shows two emission maxima at 479 and 505 nm. Above pH 8.0, these bands start to shift to longer wavelength (λ_{max} 492 nm) and increase in intensity up to about pH 10.9, above which the intensity remains essentially constant. The overall increase in intensity at 492 nm is by a factor of *ca.* 1.6, and the pK_a was 9.0, smaller than that, 11.6, of the free ligand **HL$_1$**.[17] Spectral changes for **3cL$_{2-3}$** as a function of pH are displayed in Fig. S17 and 18.† The emission intensity and wavelength of both complexes were relatively unaffected over the pH range from *ca.* 4 to 7.5. Further increases in pH led to a gradual increase in intensity by a factor of *ca.* 1.8 and 1.7 for **3cL$_2$** and **3cL$_3$**, respectively. The pK_a values of complexes **3cL$_{2-3}$** are *ca.* 8.0 and 9.0, respectively, again, smaller than the ground state pK_a of the free ligands (12.3 for **HL$_2$** and 11.6 for **HL$_3$**).[17]

Overall, the phenylpyridine complexes **3cL$_{1-3}$** show an increase in emission intensity with increasing pH, which is the opposite trend to that observed for the phenylpyrazole complexes **3aL$_{1-3}$** described above. This suggests that different molecular orbitals are involved in the emission from the two series of complexes. The pK_a values for the phenylpyridine complexes are lower than those for the phenylpyrazole complexes for L_1 and L_2 (by approximately 1 and 2 units respectively) whilst that for L_3 is about the same. However, the pK_a values are still rather high for use a biological pH sensors hence the CF_3 substituted complex **3dL$_2$** was examined and the results are shown in Fig. S19.†

For **3dL$_2$** the emission intensity decreases at high pH whilst the opposite is true for the unsubstituted complex **3cL$_2$**. Hence, as found for the phenylpyrazole complexes addition of a CF_3 substituent to the C^N ligand has the effect of reversing the slope of the pH curve. From the intensity changes a pK_a value of 7.8 was determined (Fig. S19†), which is surprisingly similar to that of the unsubstituted complex (pK_a 8.0 for **3cL$_2$**).

Conclusions

In conclusion, for all the complexes studied changes in pH gave only very minor changes in the associated UV-vis spectra over the full pH range studied. Hence, determining the ground state pK_a was not feasible. In contrast, the emission intensity of the complexes was significantly modulated (by a factor of 1.2 to 2.9) by altering the pH. Surprisingly the phenylpyrazole complexes **3aL$_{1-3}$** showed an intensity decrease with increasing pH (switch off) whilst the phenylpyridine complexes **3cL$_{1-3}$** showed an increase in emission intensity with increasing pH. Changing the R group on the N^N ligand had an effect of up to 1 pH unit on the subsequent pK_a values. However, the trends were not the same for the different series of complexes. More surprisingly, putting CF_3 groups on the cyclometallated phenyls, *i.e.*, complexes **3bL$_{1-3}$** and **3dL$_2$**, resulted in a complete reversal in the direction of the intensity change when compared to their respective unsubstituted congeners. The unsubstituted complexes had pK_a values ranging from 8.0 to 10.0 and as anticipated, adding the electron-withdrawing group reduced the pK_a of the complexes to 6.8–7.8, thereby extending to useful pK_a range.

However, whilst adding CF_3 substituents had the desired effect on the pK_a, in general it tended to reduce the proportional change in emission intensity per unit change in pH. The reason(s) for this difference are not currently known. It is hoped that these studies will provide useful information for the design of other pH sensitive cyclometallated iridium complexes.

Experimental

All reactions were carried out under an inert atmosphere of nitrogen unless otherwise mentioned though all work-up was carried out in air. Microwave reactions were carried out in a CEM Explorer hybrid 12 microwave synthesiser, solutions were degassed by bubbling nitrogen through the solution for 3 minutes before sealing the tube with a plastic cap. NMR spectra were recorded on a Bruker DRX400 spectrometer operating at 400.13 (^{1}H), 376.50 (^{19}F), 100.61 MHz (^{13}C) and or a Bruker DRX500 spectrometer at 500 (^{1}H) and 125 MHz (^{13}C) respectively at ambient temperature; chemical shifts (ppm) are referred to the residual protic solvent peaks and coupling constants are expressed in Hertz (Hz). Assignments of ^{1}H and ^{13}C NMR signals were made where possible, using COSY, NOESY, TOCSY, HMQC, HMBC, DEPT and APT spectra. Electrospray (ES) and ASAP mass spectra were obtained using a micromass Qtra LC spectrometer in HPLC grade MeCN. The UV/Vis spectra measurements were carried out on a Shimadzu UV-1600 series spectrometer in 1 cm quartz cuvette at room temperature. Luminescence studies were performed on a Jobin Yvon Horiba Fluoromax–P spectrofluorimeter, in either reagent grade DCM or MeOH, HPLC grade MeCN or spectroscopy grade DMF (*N*,*N*-Dimethylformamide). Complexes were excited at a wavelength between 320–405 nm using a filter of 370, 399 or 450 nm. The pH values were determined using a Jenway 3510 pH meter, calibrated prior to use with standard buffer solutions of pH 4, 6 and 10 at room temperature. The pK_a values for all complexes were determined by the change of emission intensity upon the pH changing from about *ca.* 2.5 to 12.5.

2-(1*H*-pyrazol-3-yl)pyridine ligands $\mathbf{HL_{1-3}}$ were prepared by literature methods[24] as were 1-(4-(trifluoromethyl)phenyl)-1*H*-pyrazole[25] and 2-(4-(trifluoromethyl)phenyl)pyridine[26] and the bis-cyclometallated dimers **1a–d**[18] and the data are consistent with those published.[18,19]

General procedure for the synthesis of cationic complexes [Ir(C^N)$_2$(HN^N)]PF$_6$

The relevant dimer **1a**, **c**, ligand ($\mathbf{HL_1}$/$\mathbf{HL_2}$/$\mathbf{HL_3}$) (2.2–2.4 equiv.) and KPF_6 (2.4 equiv.) were placed in a microwave vial and methanol (3 ml) was added. After degassing with nitrogen the tube was heated under microwave irradiation at 60 °C for 20–40 min. After this time, the solvent was removed *in vacuo* leaving behind a solid which was dissolved in DCM (15 ml) and passed through Celite. The filtrate was reduced in volume and hexane was added slowly to induce precipitation. The precipitate was isolated, washed with hexane and dried *in vacuo*. Samples could be recrystallised from DCM/hexane.

General procedure for the synthesis of neutral complexes [Ir(C^N)$_2$(N^N)]

A mixture of the ligand ($\mathbf{HL_1}$/$\mathbf{HL_2}$/$\mathbf{HL_3}$) (2.2–2.4 equiv.) and an equimolar amount of NaOMe in MeOH (3 ml) was warmed gently at 40 °C for 15 min. A solution of the appropriate dimer **1a–d** (1 equiv.) in DCM (6 ml) was added and the mixture was stirred for 2–4 h at room temperature. After this time, the solvent was removed *in vacuo* and the residue was dissolved in DCM (15 ml) and passed through Celite. The filtrate was reduced in volume and hexane was added slowly to induce precipitation. The precipitate was isolated, washed with hexane and dried *in vacuo*. Samples could be recrystallised from DCM/hexane.

For all complexes the crude yields after washing but before recrystallisation are reported.

Synthesis of 2a$\mathbf{HL_1}$. Using the general procedure, **2a$\mathbf{HL_1}$** was prepared from **1a** (50 mg, 0.049 mmol), $\mathbf{HL_1}$ (16 mg, 0.10 mmol) and KPF_6 (22 mg, 0.12 mmol). After work up, the compound was isolated as a grey yellow solid (58 mg, 78%), ^{1}H NMR (500 MHz, CD_3CN, 300 K): δ 8.40 (1H, d, J = 2.9 Hz, H_{5B}), 8.36 (1H, d, J = 2.9 Hz, H_{5A}), 8.20 (1H, dt, J = 7.9, 0.9 Hz, H_e), 8.10 (1H, td, J = 7.9, 1.7 Hz, H_f), 8.01 (1H, ddd, J = 5.5, 1.7, 0.8 Hz, H_h), 7.83 (1H, d, J = 2.9 Hz, H_a), 7.50 (1H, dd, J = 4.7, 1.0 Hz, H_{4B}), 7.47 (1H, dd, J = 4.7, 1.0 Hz, H_{4A}), 7.37 (1H, ddd, J = 7.7, 5.5, 1.3 Hz, H_g), 7.20 (1H, d, J = 2.9 Hz, H_b), 7.11–7.03 (3H, m, $H_{3A,3B,7B}$), 7.01 (1H, d, J = 2.2 Hz, H_{7A}), 6.90 (1H, td, J = 7.5, 1.2 Hz, H_{2B}), 6.85 (1H, td, J = 7.5, 1.2 Hz, H_{2A}), 6.62 (1H, t overlapping, J = 2.7 Hz, H_{6B}), 6.61 (1H, t overlapping, J = 2.7 Hz, H_{6A}), 6.32 (1H, dd, J = 5.0, 1.3 Hz, H_{1B}), 6.30 (1H, dd, J = 5.1, 1.3 Hz, H_{1A}). ^{13}C NMR (125 MHz, CD_3CN, 300 K): δ 154.0 (C_c), 153.3 (C_d), 151.8 (C_h), 144.8 ($C_{9A/9B}$), 144.6 ($C_{9A/9B}$), 140.6 (C_f), 140.1 (C_{7A}), 139.7 (C_{7B}), 135.0 (C_a), 134.4 ($C_{1A/1B}$), 134.1 ($C_{1A/1B}$), 132.4 ($C_{8A/8B}$), 128.8 (C_{5B}), 128.7 (C_{5A}), 128.6 ($C_{8A/8B}$), 127.5 ($C_{2A/2B}$), 127.1 ($C_{2A/2B}$), 127.0 (C_g), 124.3 ($C_{3A/3B}$), 124.2 ($C_{3A/3B}$), 123.9 (C_e), 113.0 (C_{4B}), 112.7 (C_{4A}), 109.3 ($C_{6A/6B}$), 109.1 ($C_{6A/6B}$), 106.3 (C_b). HRMS (ASAP): m/z 624.1497 [624.1488 calculated for $C_{26}H_{21}{}^{193}IrN_7$].

Synthesis of 2a$\mathbf{HL_2}$. This was prepared from dimer **1a** (71 mg, 0.07 mmol) $\mathbf{HL_2}$ (31 mg, 0.154 mmol) and KPF_6 (31 mg, 0.168 mmol). After work up, the compound was isolated as a yellow solid (107 mg, 93%). ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K): δ 8.20 (1H, d, J = 2.5 Hz, H_{5B}), 8.13 (1H, d, J = 2.5 Hz, H_{5A}), 8.07–7.98 (3H, m, $H_{e,f,h}$), 7.38 (1H, dd, J = 8.0, 0.9 Hz, H_{4B}), 7.33–7.28 (2H, m, H_{4A} H_g), 7.08 (2H, 2 × td, J = 7.6, 1.3 Hz, $H_{3A,3B}$), 6.93 (1H, br. d, J = 1.8 Hz, H_{7B}), 6.91–6.84 (4H, m, H_{2B}, H_{2A}, H_b, H_{7A}), 6.60 (1H, t, J = 2.6 Hz, H_{6B}), 6.58 (1H, t, J = 2.6 Hz, H_{6A}), 6.37 (1H, dd, J = 7.6, 1.2 Hz, H_{1B}), 6.27 (1H, dd, J = 7.6, 1.2 Hz, H_{1A}), 1.35 (9H, s, H^t_{Bu}). ^{13}C NMR (125 MHz, CD_2Cl_2, 300 K): δ 159.2 (C_a), 153.4 (C_q), 152.9 (C_q), 151.0 (C_h), 144.0 (C_q), 143.8 (C_q), 139.9 (C_f), 139.1 (C_{7A}), 138.7 (C_{7B}), 127.2 (C_{5B}), 126.7 (C_{5A}), 134.3 (C_{1B}), 133.5 (C_{1A}), 130.8 ($C_{9A/9B}$), 128.6 ($C_{9A/9B}$), 127.5 ($C_{2A/2B}$), 127.4 ($C_{2A/2B}$), 126.2 (C_g), 123.9 ($C_{3A/3B}$), 123.8 ($C_{3A/3B}$), 123.0 (C_e), 112.2 (C_{4A}), 112.1 (C_{4B}), 108.7 (C_{6A}), 108.5 (C_{6B}), 102.2 (C_b), 32.1 (C_i), 30.0 (Ct_{Bu}). HRMS (ASAP): m/z 680.2145 [680.2114 calculated for $C_{30}H_{29}{}^{193}IrN_7$].

Synthesis of 2a$\mathbf{HL_3}$. This was prepared from dimer **1a** (50 mg, 0.046 mmol) $\mathbf{HL_3}$ (23 mg, 0.11 mmol) and KPF_6 (21 mg, 0.12 mmol). After work up, the crude material was purified by column chromatography on silica gel DCM/ethyl acetate (2 : 1) to give a grey yellowish solid (68 mg, 82%). ^{1}H NMR (500 MHz, CD_3CN, 298 K): δ 8.41 (1H, d, J = 2.7 Hz, H_{5B}), 8.36 (1H, d, J = 2.7 Hz, H_{5A}), 8.22 (1H, br. d, J = 7.8 Hz, H_e),

8.10 (1H, td, J = 7.8, 1.1 Hz, H_f), 7.99 (1H, br. d, J = 5.3 Hz, H_h), 7.74 (2H, br. d, J = 6.9 Hz, $H_{j,k}$), 7.55–7.46 (6H, m, $H_{b,l,m,n,4A,4B}$), 7.38 (1H, br. t, J = 6.2 Hz, H_g), 7.21 (1H, d, J = 2.1 Hz, H_{7A}), 7.10–7.04 (3H, m, $H_{3A,3B,7B}$), 6.89 (1H, t J = 7.3 Hz, $H_{2A/2B}$), 6.86 (1H, t J = 7.3 Hz, $H_{2A/2B}$), 6.63 (1H, t, J = 2.5 Hz, H_{6A}), 6.61 (1H, t, J = 2.5 Hz, H_{6B}), 6.32 (1H, d, J = 7.3 Hz, H_{1B}), 6.28 (1H, d, J = 7.3 Hz, H_{1A}). ^{13}C NMR: (125 MHz, CD_3CN, 298 K): δ 155.0 (C_q), 153.2 (C_q), 151.6 (C_h), 149.0 (C_q), 145.0 (C_q), 144.6 (C_q), 140.7 (C_f), 140.3 (C_{7A}), 139.7 (C_{7B}), 135.3 ($C_{1A/1B}$), 134.0 ($C_{1A/1B}$), 132.2 (C_q), 130.8 (C_n), 130.2 ($2C_{l,m}$), 129.0 (C_q), 128.8 (C_{5A}), 128.7 (C_{5B}), 128.4 (C_q), 127.7 ($2C_{j,k}$), 127.5 ($C_{2A/2B}$), 127.2 ($C_{2A/2B}$), 127.0 (C_g), 124.4 ($C_{3A/3B}$), 124.1 ($C_{3A/3B}$), 124.0 (C_e), 113.0 ($C_{4A/4B}$), 112.6 ($C_{4A/4B}$), 109.3 (C_{6B}), 109.1 (C_{6A}), 104.0 (C_b). HRMS (ASAP): m/z 700.1821 [700.1801 calculated for $C_{32}H_{25}{}^{193}IrN_7$].

Synthesis of 3aL$_1$. This was prepared from dimer **1a** (50 mg, 0.08 mmol), **HL$_1$** (16 mg, 0.11 mmol) and NaOMe (5 mg, 0.11 mmol). After work up, the crude product was purified by column chromatography (aluminium oxide); the product was eluted with CH_2Cl_2/MeOH (30 : 1), respectively. **3aL$_1$** was isolated as a grey yellow solid (45 mg, 76%). ^{1}H NMR: (500 MHz, CD_3CN, 298 K): δ 8.29 (1H, d, J = 2.7 Hz, H_{5B}), 8.26 (1H, d, J = 2.7 Hz, H_{5A}), 7.90–7.86 (2H, m Hz, $H_{h,e}$), 7.83 (1H, td, J = 7.7, 1.5 Hz, H_f), 7.47 (1H, d, J = 2.1 Hz, H_a), 7.39 (1H, d, J = 7.6 Hz, H_{4A}), 7.35 (1H, d, J = 7.8 Hz, H_{4B}), 7.06 (1H, ddd, J = 7.6, 5.6, 1.2 Hz, H_g), 7.00–6.95 (2H, m, H_{7B}, H_{3A}), 6.91 (1H, td, J = 7.7, 1.1 Hz, H_{3B}), 6.82–6.80 (2H, m, H_b, H_{2A}), 6.72–6.69 (2H, m, $H_{2B,7A}$), 6.53 (1H, t, J = 2.5 Hz, H_{6B}), 6.50 (1H, t, J = 2.5 Hz, H_{6A}), 6.34 (1H, dd, J = 7.3, 1.0 Hz, H_{1A}), 6.22 (1H, dd, J = 7.4, 1.0 Hz, H_{1B}). ^{13}C NMR (125 MHz, MeOD, 298 K): δ 154.4 (C_c), 154.1 (C_d), 151.7 (C_h), 145.2 ($C_{8A/8B}$), 145.1 ($C_{8A/8B}$), 140.9 (C_f), 140.0 ($C_{7A/7B}$), 139.5 ($C_{7A/7B}$), 135.2 (C_{1B}), 134.9 (C_a), 134.4 (C_{1A}), 132.7 ($C_{9A/9B}$), 129.2 ($C_{9A/9B}$), 128.9 (C_{5A}), 128.8 (C_{5B}), 127.7 ($C_{2A/2B}$), 127.3 ($C_{2A/2B}$), 127.1 (C_g), 124.5 ($C_{3A/3B}$), 124.3 ($C_{3A/3B}$), 124.0 (C_e), 113.0 ($C_{4A/4B}$), 112.8 ($C_{4A/4B}$), 109.5 ($C_{6A/6B}$), 109.3 ($C_{6A/6B}$), 106.4 (C_b). HRMS (ASAP): $[M + H]^+$, m/z 624.1489 [624.1488 calculated for $C_{26}H_{21}{}^{193}IrN_7$].

Synthesis of 3aL$_2$. This was prepared from dimer **1a** (71 mg, 0.069 mmol), **HL$_2$** (31 mg, 0.15 mmol) and NaOMe (30 mg, 0.15 mmol) in MeOH (3 ml) and DCM (6 ml), and was allowed to stir for 2.5 h. After work up, **3aL$_2$** was isolated as grey yellow solid (73 mg, 76%). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 7.93 (1H, d, J = 2.9 Hz, $H_{5A/B}$), 7.84 (2H, br. m, $H_{5A/B,h}$), 7.63 (1H, br. d, J = 7.4 Hz, H_e), 7.60 (1H, td, J = 7.7, 1.3 Hz, H_f), 7.15 (1H, d, J = 7.7 Hz, $H_{4A/B}$), 7.11 (1H, d, J = 7.6 Hz, $H_{4A/B}$), 6.91 (1H, td, J = 7.6, 1.1 Hz, H_{3B}), 6.86 (1H, td, J = 7.6, 0.8 Hz, H_{3A}), 6.82–6.72 (5H, m, $H_{2A,2B,7B,g,7A}$), 6.49 (1H, s, H_b), 6.37 (1H, t, J = 2.4 Hz, $H_{6A/B}$), 6.33 (1H, dd, J = 7.6, 1.1 Hz, H_{1A}), 6.30 (1H, dd, J = 7.5, 1.1 Hz, H_{1B}), 6.20 (1H, t, J = 2.4 Hz, $H_{6A/B}$), 1.29 (9H, s, $H^t{}_{Bu}$). ^{13}C NMR: (125 MHz, $CDCl_3$, 300K): δ 163.9 (C_q), 157.2 (C_q), 149.5 (C_q), 149.4 (CH), 144.1 (C_q), 143.3 (C_q), 138.7 (CH), 137.3 (CH), 137.1 (C_q), 136.8 (CH), 134.0 ($C_{1A/1B}$), 133.7 ($C_{1A/1B}$), 133.0 (C_q), 126.3 (CH), 126.0 (CH), 125.6 (CH), 125.4 (CH), 122.0 (CH), 121.5 (CH), 120.7 (CH), 119.0 (CH), 111.1 (CH), 110.8 (CH), 107.3 (CH), 107.0 (CH), 98.8 (C_b), 32.2 (C_i), 31.2 ($C^t{}_{Bu}$). HRMS (ASAP): $[M + H]^+$, m/z 680.2115 [680.2114 calculated for $C_{30}H_{29}{}^{193}IrN_7$].

Synthesis of 3aL$_3$. This was prepared from dimer **1a** (50 mg, 0.048 mmol), **HL$_3$** (23.7 mg, 0.11 mmol) and NaOMe (6 mg, 0.11 mmol) in MeOH (3 ml) and DCM (6 ml). After work up, the compound was isolated as a pale yellow solid (47 mg, 69%). ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ 8.01 (1H, dd, J = 3.0, 0.4 Hz, H_{5A}), 7.94 (1H, dd, J = 2.9, 0.4 Hz, H_{5B}), 7.82 (1H, ddd, J = 5.5, 1.4, 0.8 Hz, H_h), 7.70–7.67 (3H, m, $H_{e,j,k}$), 7.63 (1H, td, J = 7.7, 1.2 Hz, H_f), 7.23–7.16 (4H, m, $H_{4A,4B,l,m}$), 7.09–7.05 (1H, m, Hz, H_n), 6.95 (1H, s, H_b), 6.92 (1H, td, J = 7.7, 1.3 Hz, H_{3A}), 6.90 (1H, td, J = 7.7, 1.3 Hz, H_{3B}), 6.85 (1H, d, J = 1.6 Hz, H_{7A}), 6.84–6.80 (2H, m, $H_{7B,g}$), 6.76 (1H, td, J = 7.4, 1.2 Hz, H_{2A}), 6.73 (1H, td, J = 7.4, 1.2 Hz, H_{2B}), 6.40 (1H, t, J = 2.5 Hz, H_{6B}), 6.35 (1H, t, J = 2.5 Hz, H_{6A}), 6.33 (1H, dd, J = 7.4, 1.2 Hz, H_{1A}), 6.28 (1H, dd, J = 7.5, 1.1 Hz, H_{1B}). ^{13}C NMR (125 MHz, CD_2Cl_2, 298 K): δ 157.1 (C_q), 153.6 (C_q), 152.0 (C_q), 150.1 (C_h), 144.5 (C_q), 143.6 (C_q), 139.1 (C_{7B}), 138.2 (C_f), 137.6 (C_q), 137.5 (C_{7A}), 136.1 (C_q), 134.3 (C_{1A}), 134.1 (C_{1B}), 133.7 (C_q), 128.7 ($2C_{l/m}$), 126.6 (CH), 126.4 (2CH), 126.2 (CH), 126.0 (CH), 125.4 ($2C_{j,k}$), 122.5 ($C_{2A/2B}$), 121.8 ($C_{2A/2B}$), 121.7 (C_g), 119.7 (CH), 111.4 ($C_{4A/4B}$), 111.3 ($C_{4A/4B}$), 107.8 (C_{6A}), 107.5 (C_{6B}), 100.7 (C_b). HRMS (ASAP): $[M + H]^+$, m/z 700.1818 [700.1801 calculated for $C_{32}H_{25}{}^{193}IrN_7$].

Synthesis of 3bL$_1$. This was prepared from the dimer **1b** (60 mg, 0.046 mmol), **HL$_1$** (14.7 mg, 0.101 mmol) and NaOMe (12 mg, 0.22 mmol). After work up gave **3bL$_1$** a grey yellow solid (65 mg, 92%). ^{1}H NMR (500 MHz, DMSO, 298 K): δ 8.96 (1H, d, J = 3.0 Hz, $H_{5A/5B}$), 8.95 (1H, d, J = 3.0 Hz, $H_{5A/5B}$), 7.95 (1H, brd, J = 7.3 Hz, H_e), 7.90(1H, td, J = 7.3, 1.2 Hz, H_f) 7.86 (1H, d, J = 8.3 Hz, $H_{4A/4B}$) 7.80 (1H, d, J = 8.3 Hz, $H_{4A/4B}$) 7.70 (1H, d, J = 5.4 Hz, H_h) 7.36 (1H, dd, J = 7.2, 1.7 Hz, H_{3A}) 7.34 (1H, d, J = 2.0 Hz, H_a) 7.27 (1H, dd, J = 1.4, 8.4 Hz, H_{3B}), 7.21 (1H, d, J = 2.2 Hz, H_{7B}), 7.16 (1H, br. t, J = 5.8 Hz, H_g), 6.81 (1H, d, J = 1.9 Hz, H_b), 6.76 (1H, br. t, J = 4.0 Hz, H_{6A}), 6.73 (1H, br. t, J = 2.0 Hz, H_{6B}), 6.68 (1H, d, J = 2.0 Hz, H_{7A}), 6.51 (1H, d, J = 1.8 Hz, H_{1A}), 6.35 (1H, d, J = 1.6 Hz, H_{1B}). ^{13}C NMR (126 MHz, DMSO, 298 K): δ 155.8 (C_q), 149.0 (C_q), 148.9 (CH), 147.1 (C_q), 146.2 (C_q), 139.7 (CH), 139.1 (CH), 138.9 (CH), 138.3 (C_q), 133.9 (C_q), 129.4 (CH), 128.9 (CH), 128.9 (CH), 128.5 (CH), 122.2 (CH), 120.0 (CH), 119.5 (CH), 119.0 (CH), 111.9 (CH), 111.3 (CH), 108.9 (CH), 108.7 (CH), 103.6 (CH), the CCF_3 carbons were not identified due to low signal-to-noise ratios. ^{19}F NMR (376 MHz, DMSO, 298 K): δ −61.73 (s), −61.86 (s). HRMS (ESI): $[M + H]^+$, m/z 760.1267 [760.1236 calculated for $C_{28}H_{19}F_6{}^{193}IrN_7$].

Synthesis of 3bL$_2$. This was prepared from dimer **1b** (70 mg, 0.054 mmol), **HL$_2$** (24.0 mg, 0.118 mmol), NaOMe (13 mg, 0.236 mmol). After work up gave **3bL$_2$** as a pale yellow solid (61 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.40 (1H, d, J = 2.2 Hz, H_{5B}), 8.33 (1H, d, J = 2.9 Hz, H_{5A}), 8.02 (1H, br. d J = 7.7 Hz, H_e), 7.97 (1H, br. t, J = 7.6 Hz, H_f), 7.82 (1H, br. d, J = 5.2 Hz, H_h), 7.51 (1H, d, J = 7.9 Hz, H_{4B}), 7.46 (1H, d, J = 8.3 Hz, H_{4A}), 7.25–7.21 (2H, m, $H_{3A,g}$), 7.17 (1H, br. d, J = 7.7 Hz, H_{3B}), 7.02 (1H, d, J = 2.1 Hz, H_{7A}), 6.82 (1H, d, J = 2.2 Hz, H_{7B}), 6.74 (1H, s, H_b), 6.57 (1H, t, J = 2.6 Hz, H_{6A}), 6.47 (1H, t, J = 2.3 Hz, H_{6B}), 6.43 (1H, br. d, J = 1.2 Hz, H_{1A}), 6.40 (1H, br. d, J = 0.6 Hz, H_{1B}), 1.36 (9H, s, $H^t{}_{Bu}$). ^{13}C NMR (125 MHz, $CDCl_3$,

298 K): δ 160.1 (C_q), 153.4 (C_q), 151.3 (C_q), 150.0 (CH), 145.8 (q), 140.2 (CH), 139.3 (CH), 138.3 (CH), 132.0 (C_q), 130.1 (CH), 129.4 (CH), 129.0 (CH), 128.3 (C_q), 128.2 (C_q), 128.1 (CH), 127.5 (C_q), 127.3 (C_q), 125.0 (CH), 122.1 (CH), 121.1 (CH), 120.9 (CH), 112.4 (CH), 111.7 (CH), 109.1 (CH), 108.4 (CH), 101.2 (C_b), 32.0 (C_i), 30.2 (C^t_{Bu}). The CCF_3 carbons were not identified due to low signal-to-noise ratios. ^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ −61.73 (s), −62.00 (s). HRMS (ESI): $[M + H]^+$ *m*/*z* 816.1871 [816.1861 calculated for $C_{32}H_{27}F_6{}^{193}IrN_7$].

Synthesis of 3bL$_3$. This was prepared from dimer **1b** (70 mg, 0.053 mmol), **HL$_3$** (26.2 mg, 0.12 mmol) and NaOMe (12.7 mg, 0.23 mmol). After work up gave **3bL$_3$** as a pale yellow solid (77 mg, 85%). ^{1}H NMR (400 MHz, DMSO, 298 K): δ 8.99 (1H, d, *J* = 2.8 Hz, H_{5B}), 8.95 (1H, d, *J* = 2.5 Hz, H_{5A}), 8.00 (1H, br. d, *J* = 8.0 Hz, H_e), 7.94 (1H, td, *J* = 7.5, 1.5 Hz, H_f), 7.86 (1H, d, *J* = 8.2 Hz, H_{4A}), 7.82 (1H, d, *J* = 8.2 Hz, H_{4B}), 7.71 (1H, br d, *J* = 5.0 Hz, H_h), 7.66–7.61 (2H, m, $H_{j,k}$), 7.36 (1H, dd, *J* = 8.5, 1.5 Hz, H_{3A}), 7.31–7.23 (5H, m, $H_{3B,7B,b,l,m}$), 7.18 (1H, ddd, *J* = 6.5, 5.5, 1.5 Hz, H_g), 7.12 (1H, br t, *J* = 7.0 Hz, H_n), 6.84 (1H, d, *J* = 2.2 Hz, H_{7A}), 6.77 (1H, t, *J* = 2.5 Hz, H_{6B}), 6.71 (1H, t, *J* = 2.5 Hz, H_{6A}), 6.47 (1H, br. d, *J* = 1.5 Hz, H_{1A}), 6.40 (1H, br. d, *J* = 1.6 Hz, H_{1B}). ^{13}C NMR (126 MHz, DMSO, 298 K): δ 155.5 (C_q), 152.0 (C_q), 151.0 (C_q), 149.0 (C_h), 147.0 (C_q), 146.2 (C_q), 139.4 (C_f), 139.0 (2 × $C_{7A,7B}$), 138.2 (C_q), 135.3 (C_q), 133.8 (C_q), 129.4 ($C_{5A/B}$), 129.0 ($C_{5A/B}$), 128.8 ($C_{1A/B}$), 128.6 ($C_{1A/B}$), 128.3 (2 × $C_{l,m}$), 125.7 (C_n), 124.4 (2 × $C_{j/k}$), 122.4 (C_g), 120.0 (C_{3A}), 119.6 (C_e), 119.0 (C_{3B}), 111.9 (C_{4A}), 111.4 (C_{4B}), 109.0 (C_{6B}), 108.8 (C_{6A}), 100.8 (C_b). The CCF_3 carbons were not identified due to low signal-to-noise ratios. ^{19}F NMR (376 MHz, DMSO, 298 K): δ −60.24 (s), −60.37 (s). HRMS (ESI): $[M + H]^+$, *m*/*z* 836.1589 [836.1549 calculated for $C_{34}H_{23}F_6{}^{193}IrN_7$].

Synthesis of 2cHL$_1$. This was prepared from dimer **1c** (50 mg, 0.048 mmol), **HL$_1$** (16 mg, 0.10) and KPF_6 (21.5 mg, 0.12 mmol) in MeOH (3 ml) were heated in a microwave irradiation for 40 min. After work up, the product was isolated as an yellow solid (53 mg, 72%). ^{1}H NMR (500 MHz, CD_3CN, 298 K): δ 8.20 (1H, dt, *J* = 7.8, 1.1 Hz, H_e), 8.08 (1H, d, *J* = 8.09 Hz, H_{5B}), 8.05 (2H, m, $H_{5A,f}$), 7.90–7.86 (2H, m, $H_{6A,6B}$), 7.84 (1H, ddd, *J* = 6.0, 1.5, 0.9 Hz, H_h), 7.81 (1H, d, *J* = 1.1 Hz, H_{4A}), 7.79–7.78 (2H, m, $H_{4B,a}$), 7.66 (1H, ddd, *J* = 5.9, 1.5, 0.7 Hz, H_{8B}), 7.61 (1H, ddd, *J* = 5.8, 1.4, 0.7 Hz, H_{8A}), 7.35 (1H, ddd, *J* = 7.6, 5.5, 1.4 Hz, H_g), 7.18 (1H, d, *J* = 2.7 Hz, H_b), 7.11–7.01 (4H, m, $H_{3A,3B,7A,7B}$), 6.92 (1H, td, *J* = 7.5, 1.4 Hz, H_{2A}), 6.88 (1H, td, *J* = 7.4, 1.3 Hz, H_{2B}), 6.32 (1H, dd, *J* = 7.6, 0.6 Hz, H_{1B}), 6.29 (1H, dd, *J* = 7.6, 0.7 Hz, H_{1A}). ^{13}C NMR (125 MHz, CD_3CN, 298 K): δ 168.8 (C_q), 168.4 (C_q), 153.2 (C_q), 153.0 (C_q), 151.3 (C_h), 150.8 (C_q), 150.7 (C_{8A}), 150.4 (C_{8B}), 147.1 (C_q), 145.7 (C_q), 145.5 (C_q), 140.5 (C_f), 139.5 ($C_{6A/6B}$), 139.4 ($C_{6A/6B}$), 135.0 (C_a), 133.3 (C_{1A}), 132.5 (C_{1B}), 131.3 (C_{2B}), 130.8 (C_{2A}), 127.4 (C_g), 125.8 (C_{4A}), 125.6 (C_{4B}), 124.6 (C_e), 124.3 ($C_{3A/3B/7A/7B}$), 124.0 ($C_{3A/3B/7A/7B}$), 123.6 ($C_{3A/3B/7A/7B}$), 123.4 ($C_{3A/3B/7A/7B}$), 120.7 (C_{5A}), 120.5 (C_{5B}), 106.4 (C_b). HRMS (ASAP): *m*/*z* 646.1584 [646.1583 calculated for $[C_{30}H_{23}{}^{193}IrN_5]$].

Synthesis of 2cHL$_2$. This was prepared from dimer **1c** (50 mg, 0.046 mmol), **HL$_2$** (21 mg, 0.10) and KPF_6 (21 mg, 0.11 mmol) in MeOH (3 ml). After work up, the compound was isolated as a yellow solid (73 mg, 92%). ^{1}H NMR (500 MHz, CD_3CN, 300 K): δ 8.15 (1H, dt, *J* = 7.9, 0.8 Hz, H_e), 8.09 (1H, tt, *J* = 7.9, 0.8 Hz, H_{5B}), 8.06–8.01 (2H, m, $H_{5A,f}$), 7.91 7.84 (2H, m, $H_{6A,6B}$), 7.81–7.76 (2H, m, $H_{h,4B}$), 7.77 (1H, d, *J* = 7.6 Hz, H_{4A}), 7.65 (1H, br. d, *J* = 5.8, Hz, H_{8B}), 7.58 (1H, br. d, *J* = 5.8 Hz, H_{8A}), 7.33 (1H, br. t, *J* = 6.6 Hz, H_g), 7.13–7.11 (1H, m, H_{7A}), 7.09–6.99 (4H, m, $H_{3A,3B,7B,b}$), 6.91 (1H, td, *J* = 7.4, 1.2 Hz, H_{2A}), 6.87 (1H, td, *J* = 7.4, 1.1 Hz, H_{2B}), 6.30 (1H, dd, *J* = 7.6, 0.8 Hz, H_{1B}), 6.23 (1H, dd, *J* = 7.5, 0.8 Hz, H_{1A}), 1.34 (9H, s, H^t_{Bu}). ^{13}C NMR: (125 MHz, CD_3CN, 298 K) : δ 169.3 (C_q), 168.6 (C_q), 160.4 (C_q), 153.6 (C_q), 153.4 (C_q), 151.4 (C_h), 151.0 (C_{8A}), 150.7 (C_{8B}), 150.0 (C_q), 148.0 (C_q), 146.1 (C_q), 146.0 (C_q), 141.0 (C_f), 139.8 ($C_{6A/6B}$), 139.7 ($C_{6A/6B}$), 134.0 (C_{1B}), 132.6 (C_{1A}), 131.7 (C_{2A}), 131.1 (C_{2B}), 127.8 (C_g), 126.1 ($C_{4A/4B}$), 126.0 ($C_{4A/4B}$), 125.0 (C_{7A}), 124.6 ($C_{3A/3B/7B}$), 124.2 (C_e), 124.0 ($C_{3A/3B/7B}$), 123.7 ($C_{3A/3B/7B}$), 121.1 (C_{5A}), 120.8 (C_{5B}), 103.5 (C_b), 32.9 (C_i), 30.7 (C^t_{Bu}). HRMS (ASAP): *m*/*z* 702.2244 [702.2209 calculated for $C_{34}H_{31}{}^{193}IrN_5$].

Synthesis of 2cHL$_3$. This was prepared from dimer **1c** (50 mg, 0.046 mmol), **HL$_3$** (23.5 mg, 0.10) and KPF_6 (20.4 mg, 0.11 mmol) in MeOH (3 ml). After work up, the compound was isolated as a yellow solid (68 mg, 84%). ^{1}H NMR (500 MHz, CD_3CN, 298 K): δ 8.23 (1H, dt, *J* = 7.8, 1.1 Hz, H_e), 8.11–8.09 (1H, m, H_{5B}), 8.08–8.06 (1H, m, H_f), 8.05 (1H, dd, *J* = 1.2 Hz, H_{5A}), 7.89–7.85 (3H, m, $H_{6A,6B,8A}$), 7.83 (1H, ddd, *J* = 5, 1.6, 0.8 Hz, H_h), 7.82–7.78 (2H, m, $H_{4A,4B}$), 7.72–7.71 (2H, m, $H_{j/k}$), 7.68 (1H, ddd, *J* = 5.9, 1.4, 0.63 Hz, H_{8B}), 7.52 (1H, s, H_b), 7.52–7.46 (3H, m, $H_{l,m,n}$), 7.36 (1H, ddd, *J* = 7.6, 5.5, 1.4 Hz, H_g), 7, 13–7.01 (4H, m, $H_{3A,3B,7A,7B}$), 6.93 + 6.90 (2H, 2 × td, *J* = 7.6, 0.9 Hz, $H_{2A,2B}$), 6.35 (1H, dd, *J* = 7.6, 0.9 Hz, H_{1A}), 6.27 (1H, dd *J* = 7.6, 0.8 Hz, H_{1B}). ^{13}C NMR (125 MHz, CD_3CN, 298 K): δ 169.0 (C_q), 168.2 (C_q), 154.3 (C_q), 152.8 (C_q), 151.2 ($C_{8A/h}$), 151.1 ($C_{8A/h}$), 150.4 (C_{8B}), 150.3 (C_q), 149.3 (C_q), 147.5 (C_q), 146.0 (C_q), 145.5 (C_q), 140.6 (C_{5B}), 140.4 (C_{5A}), 139.5 ($C_{6A/6B}$), 139.4 ($C_{6A/6B}$), 133.5 (C_{1B}), 132.4 (C_{1A}), 131.3 ($C_{2A/2B}$), 131.5 ($C_{2A/2B}$), 131.9 ($C_{l/m/n}$), 130.7 ($C_{l/m/n}$), 130.2 ($C_{j/k}$), 128.6 (C_q), 127.6 ($C_{l/m/n}$), 127.5 (C_g), 125.8 ($C_{4A/4B}$), 125.6 ($C_{4A/4B}$), 124.6 ($C_{j/k}$), 124.3 (C_f), 124.0 (C_e), 123.6 ($C_{3A/3B/7A/7B}$), 123.4 ($C_{3A/3B/7A/7B}$), 120.7 ($C_{3A/3B/7A/7B}$), 120.5 ($C_{3A/3B/7A/7B}$), 104.2 (C_b). HRMS (ASAP): *m*/*z* 722.11901 [722.1896 calculated for $C_{36}H_{27}{}^{193}IrN_5$].

Synthesis of 3cL$_1$. This was prepared from dimer **1c** (50 mg, 0.046 mmol), **HL$_1$** (15 mg, 0.10 mmol) and NaOMe (6 mg, 0.10 mmol) in MeOH (3 mL) and DCM (6 ml). After work up, the compound was isolated as grey yellow solid (50 mg, 83%). ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ 7.80 (1H, bd, *J* = 8.0 Hz, H_{5B}), 7.76 (1H, bd, *J* = 8.0 Hz, H_{5A}), 7.73 (1H, dt, *J* = 7.9, 1.1 Hz, H_e), 7.66 (1H, dd, *J* = 7.5, 1.6 Hz, H_f), 7.64 (1H, m, H_h), 7.60–7.56 (4H, m, $H_{4A,4B,6A,6B}$), 7.52 (1H, dd, *J* = 5.8, 0.7 Hz, H_{8B}), 7.47 (1H, m, H_{8A}), 7.46 (1H, d, *J* = 1.9 Hz, H_a), 6.92–6.90 (1H, m, H_g), 6.89–6.87 (1H, m, H_{3B}), 6.86–6.78 (4H, m, $H_{2B,3A,7A,7B}$), 6.70–6.69 (1H, m, H_{2A}), 6.68 (1H, d, *J* = 2.2 Hz, H_b), 6.27 (1H, dd, *J* = 7.5, 0.8 Hz, H_{1B}), 6.23 (1H, dd, *J* = 7.5, 0.8 Hz, H_{1A}). ^{13}C NMR (125 MHz, CD_2Cl_2, 298 K): δ 168.8 (C_q), 168.4 (C_q), 155.5 (C_q), 154.5 (C_q), 150.5 (C_q), 150.4 (C_h), 150.1

(C_{8B}), 148.9 (C_{8A}), 145.1 (C_q), 144.2 (C_q), 139.3 (C_a), 138.4 (C_f), 137.5 ($C_{6A/6B}$), 137.2 ($C_{6A/6B}$), 132.4 (C_{1B}), 132.3 (C_{1A}), 130.5 (C_{2B}), 130.0 (C_{2A}), 124.8 ($C_{4A/4B}$), 124.6 ($C_{4A/4B}$), 123.3 (C_{3B}), 123.2 ($C_{3A/7A/7B}$), 122.6 (C_g), 122.1 ($C_{3A/7A/7B}$), 121.7 ($C_{3A/7A/7B}$), 120.7 (C_e), 119.5 (C_{5B}), 119.3 (C_{5A}), 104.1 (C_b). HRMS (ASAP): $[M + H]^+$ *m*/*z* 646.1578 [656.1583 calculated for $C_{30}H_{23}{}^{193}IrN_5$].

Synthesis of 3cL$_2$. This was prepared from the **2.15c** (75 mg, 0.070 mmol), **HL$_2$** (31 mg, 0.15 mmol) and NaOMe (30 mg, 0.154 mmol) in MeOH/DCM (3 : 6 ml). After work up, the compound was isolated as yellow solid (72 mg, 73%). For the ^{1}H NMR spectrum assignments are given where possible but there are many overlapping peaks. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 7.83–7.80 (3H, m), 7.74 (1H, td, J = 7.7, 1.3 Hz, H_f), 7.66–7.58 (6H, m), 7.51 (1H, m), 6.99–6.93 (4H, m, 3 × Ph, H_g), 6.87–6.84 (3H, m), 6.61 (1H, s, H_b), 6.35 (1H, dd, J = 7.5, 0.5 Hz, H_{1B}), 6.27 (1H, dd, J = 7.5, 0.8 Hz, H_{1A}), 1.29 (9H, s, $H^t{}_{Bu}$). ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ 168.4 (C_q), 167.8 (C_q), 150.4 (CH), 149.7 (C_q), 149.5 (CH), 148.3 (CH), 144.5 (C_q), 144.0 (C_q), 138.0 (CH), 137.0 (CH), 136.7 (CH), 132.3 (CH), 131.9 (CH), 130.2 (CH), 129.8 (CH), 124.4 (CH), 124.3 (CH), 123.0 (CH), 122.9 (CH 122.1 (CH), 121.8 (CH), 121.6 (CH), 120.5 (CH), 119.2 (CH), 118.7 (CH), 100.3 (C_b), 30.7 ($C^t{}_{Bu}$). The quaternary carbon of the ^{t}Bu was not observed. HRMS (ASAP): $[M + H]^+$, *m*/*z* 702.2236 [702.2209 calculated for $C_{34}H_{31}{}^{193}IrN_5$].

Synthesis of 3cL$_3$. This was prepared from dimer **1c** (50 mg, 0.046 mmol), **HL$_3$** (23 mg, 0.10 mmol) and NaOMe (6 mg, 0.10 mmol) in MeOH/DCM (3 : 6 ml). After work up, the product was isolated as yellow solid (50 mg, 87%). The ^{1}H NMR spectrum for this complex is very complicated with a lot of overlapping signals hence very few assignments are given. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.83 (1H, bd, J = 5.5 Hz), 7.80–7.68 (5H, m), 7.66–7.52 (6H m), 7.45 (1H, td, J = 7.2, 1.1 Hz,), 7.24 (2H, t, J = 7.6 Hz), 7.11 (1H, br. t, J = 7.4 Hz), 7.01 (1H, s, H_b), 6.95 6.78 (6H, m), 6.75 (1H, td, J = 6.1, 0.9 Hz), 6.39 (1H, bd, J = 7.3 Hz, H_{1B}), 6.33 (1H, bd, J = 7.2 Hz, H_{1A}). Due to overlap no assignments are made ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ ppm 168.6 (C_q), 168.1 (C_q), 155.7 (C_q), 155.1 (C_q), 153.4 (C_q), 151.0 (C_q), 150.6 (C_q), 150.4 (CH), 149.4 (CH), 148.2 (CH), 144.6 (C_q), 143.7 (C_q), 137.5 (CH) 136.7 (CH) 136.3 (CH) 134.6 (C_q), 132.1 (CH), 132.0 (CH), 130.1 (CH), 129.5 (CH), 128.3 (2 × CH), 126.2 (CH), 125.4 (2 × CH), 124.2 (CH), 124.1 (CH), 122.6 (CH), 122.0 (CH), 121.8 (CH), 121.4 (CH), 120.9 (CH), 119.6 (CH), 119.0 (CH), 118.4 (CH), 100.9 (CH). HRMS (ASAP): $[M + H]^+$, *m*/*z* 722.1862 [722.1896 calculated for $C_{36}H_{27}{}^{193}IrN_5$].

Synthesis of 3dL$_2$. This complex was prepared from the dimer **1d** (70 mg, 0.053 mmol), **HL$_2$** (23.0 mg, 0.114 mmol) and NaOMe (13.6 mg, 0.252 mmol). After work **3dL$_2$** was isolated as a yellow solid (66 mg, 76%). ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ ppm 7.98 (1H, br d, J = 7.9 $H_{5A/5B}$) 7.90 (1H, br d, J = 8.1 Hz, $H_{5A/5B}$) 7.80–7.70 (5H, m, $H_{4A,4B,6A,6B,8B}$) 7.70–7.65 (2H, m, $H_{e,f}$) 7.54 (1H, d, J = 5.5 Hz, H_h) 7.49 (1H, d, J = 6.2 Hz, H_{8A}) 7.23 (1H, dd, J = 1.2, 8.2 Hz, H_{3A}), 7.18 (1H, dd, J = 1.2, 8.1 Hz, H_{3B}), 6.89–6.81 (2H, m, $H_{7A,7B}$), 6.86 (1H, td, J = 5.7, 2.9 Hz, H_g), 6.56 (1H, s, H_b), 6.41–6.42 (2H, overlapping, m, $H_{1A,1B}$), 1.18 (9H, s, $H^t{}_{Bu}$). ^{13}C NMR (126 MHz, CD_2Cl_2, 298 K): ^{13}C NMR (126 MHz, CD_2Cl_2, 298 K): δ 167.4 (C_q), 167.1 (C_q), 165.6 (C_q), 156.9 (C_q), 156.1 (C_q), 152.3 (C_q), 151.0 (C_{8A}), 149.8 (C_q), 149.6 (C_h), 149.5 (C_{8B}), 149.3 (C_q), 148.2 (C_q), 138.5 ($C_{f/e}$), 138.0 ($C_{6A/6B}$), 137.6 ($C_{6A/6B}$), 128.2 ($C_{1A/1B}$), 128.1 ($C_{1A/1B}$), 124.7 ($C_{4A/4B}$), 124.5 ($C_{4A/4B}$), 124.4 ($C_{7A/7B}$), 124.0 ($C_{7A/7B}$), 122.1 (C_g), 120.6 ($C_{5A/5B}$), 120.2 ($C_{5A/5B}$), 119.9 ($C_{f/e}$), 119.3 (C_{3A}), 118.4 (C_{3B}), 100.5 (C_b), 31.4 ($C^t{}_{Bu}$). The CCF_3 carbons were not observed. ^{19}F NMR (376 MHz, CD_2Cl_2, 298 K): δ −62.86 (s), −62.91 (s). HRMS (ESI): $[M + H]^+$ *m*/*z* 838.1959 [838.1956 calculated for $C_{36}H_{29}F_6{}^{193}IrN_5$].

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 (*a*) C. Y. S. Chung, S. P. Y. Li, M. W. Louie, K. K. W. Lo and V. W. W. Yam, *Chem. Sci.*, 2013, **4**, 2453–2462; (*b*) B. Tang, X. Liu, K. Xu, H. Huang, G. Yang and L. An, *Chem. Commun.*, 2007, 3726–3728; (*c*) H. R. Kermis, Y. Kostov, P. Harms and G. Rao, *Biotechnol. Prog.*, 2002, **18**, 1047–1053; (*d*) L. Cao, X. Li, S. Wang, S. Li, Y. Li and G. Yang, *Chem. Commun.*, 2014, **50**, 8787–8790; (*e*) M. Y. Wu, K. Li, Y. H. Liu, K. K. Yu, Y. M. Xie, X. D. Zhou and X. Q. Yu, *Biomaterials*, 2015, **53**, 669–678; (*f*) Y. Ge, A. Liu, J. Dong, G. Duan, X. Cao and F. Li, *Sens. Actuators, B*, 2017, **247**, 46–52.

2 (*a*) K. Qiu, Y. Chen, T. W. Rees, L. Ji and H. Chao, *Coord. Chem. Rev.*, 2019, **378**, 66–86; (*b*) S. Das, D. Saha, S. Karmakar and S. Baitalik, *J. Phys. Chem. A*, 2012, **116**, 5216–5226; (*c*) Q. Zhao, F. Li and C. Huang, *Chem. Soc. Rev.*, 2010, **39**, 3007–3030; (*d*) B. V. Harbuzaru, A. Corma, F. Rey, J. L. Jordá, D. Ananias, L. D. Carlos and J. Rocha, *Angew. Chem., Int. Ed.*, 2009, **48**, 6476–6479; (*e*) T.-T. Meng, H. Wang, Z.-B. Zheng and K.-Z. Wang, *Inorg. Chem.*, 2017, **56**, 4775–4779; (*f*) V. W. W. Yam, V. K. M. Au and S. Y. L. Leung, *Chem. Rev.*, 2015, **115**, 7589–7728; (*g*) M. Bar, D. Maity, S. Deb, S. Das and S. Baitalik, *Dalton Trans.*, 2017, **46**, 12950–12963.

3 (*a*) J. N. Demas and B. A. DeGraff, *Anal. Chem.*, 1991, **63**, 829A–837A; (*b*) J. N. Demas and B. A. DeGraff, *J. Chem. Educ.*, 1997, **74**, 690–695.

4 (*a*) B. Higgins, B. A. DeGraff and J. N. Demas, *Inorg. Chem.*, 2005, **44**, 6662–6669; (*b*) H. J. Kim, Y.-C. Jeong, J. Heo, J. I. Rhee and K.-J. Hwang, *Bull. Korean Chem. Soc.*, 2009, **30**, 539–540; (*c*) S. San Tan, S. Yanagisawa, K. Inagaki,

Y. Morikawa and M. B. Kassim, *Phys. Chem. Chem. Phys.*, 2017, **19**, 25734–25745; (*d*) H. J. Yu, Z. F. Hao, H. L. Peng, R. H. Rao, M. Sun, R. Alana, W. C. Ran, H. Chao and L. Yu, *Sens. Actuators, B*, 2017, **252**, 313–321; (*e*) F. Yu, C. Shen, T. Zheng, W. K. Chu, J. Xiang, Y. Luo, C. C. Ko, Z. Q. Guo and T. C. Lau, *Eur. J. Inorg. Chem.*, 2016, **2016**, 3641–3648.

5 (*a*) T. Mizuno, T. Fukumatsu, M. Takeuchi and S. Shinkai, *J. Chem. Soc., Perkin Trans. 1*, 2000, 407–413; (*b*) M. H. W. Lam, D. Y. K. Lee, K. W. Man and C. S. W. Lau, *J. Mater. Chem.*, 2000, **10**, 1825–1828; (*c*) M. Cattaneo, F. Fagalde, C. D. Borsarelli and N. E. Katz, *Inorg. Chem.*, 2009, **48**, 3012–3017; (*d*) T. W. Tseng, S. Mendiratta, T. T. Luo, T. W. Chen and Y. P. Lee, *Inorg. Chim. Acta*, 2018, **477**, 312–317.

6 (*a*) K. M. C. Wong, W. S. Tang, X. X. Lu, N. Zhu and V. W. W. Yam, *Inorg. Chem.*, 2005, **44**, 1492–1498; (*b*) J. L. L. Tsai, T. Zou, J. Liu, T. Chen, A. O. Y. Chan, C. Yang, C. N. Lok and C. M. Che, *Chem. Sci.*, 2015, **6**, 3823–3830.

7 M. Licini and J. A. G. Williams, *Chem. Commun.*, 1999, 1943–1944.

8 (*a*) M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson and S. R. Forrest, *Appl. Phys. Lett.*, 1999, **75**, 4–6; (*b*) M. K. Nazeeruddin, C. Klein, M. Grätzel, L. Zuppiroli and D. Berner, in *Highly Efficient OLEDs with Phosphorescent Materials*, Wiley-VCH Verlag GmbH & Co. KGaA, 2008, pp. 363–390; (*c*) C. Ulbricht, B. Beyer, C. Friebe, A. Winter and U. S. Schubert, *Adv. Mater.*, 2009, **21**, 4418–4441; (*d*) E. Longhi and L. De Cola, in *Iridium(*III*) in Optoelectronic and Photonics Applications*, ed. E. Zysman-Colman, John Wiley & Sons Ltd, 2017, pp. 205–274; (*e*) D. L. Ma, S. Lin, W. Wang, C. Yang and C. H. Leung, *Chem. Sci.*, 2017, **8**, 878–889; (*f*) V. Fernandez-Moreira, F. L. Thorp-Greenwood and M. P. Coogan, *Chem. Commun.*, 2010, **46**, 186–202; (*g*) E. Baggaley, J. A. Weinstein and J. A. G. Williams, *Coord. Chem. Rev.*, 2012, **256**, 1762–1785; (*h*) Q. Zhao, C. Huang and F. Li, *Chem. Soc. Rev.*, 2011, **40**, 2508–2524; (*i*) K. K. S. Tso and K. K. W. Lo, in *Iridium(III) in Optoelectronic and Photonics Applications*, ed. E. Zysman-Colman, John Wiley & Sons Ltd, 2017, pp. 415–477.

9 A. Nakagawa, Y. Hisamatsu, S. Moromizato, M. Kohno and S. Aoki, *Inorg. Chem.*, 2014, **53**, 409–422.

10 A. Kando, Y. Hisamatsu, H. Ohwada, T. Itoh, S. Moromizato, M. Kohno and S. Aoki, *Inorg. Chem.*, 2015, **54**, 5342–5357.

11 J. Weng, Q. Mei, W. Jiang, Q. Fan, B. Tong, Q. Ling and W. Huang, *Analyst*, 2013, **138**, 1689–1699.

12 K. Qiu, L. Ke, X. Zhang, Y. Liu, T. W. Rees, L. Ji, J. Diao and H. Chao, *Chem. Commun.*, 2018, **54**, 2421–2424.

13 M. Qian, Z. Wang, H. Qi and H. Qi, *Inorg. Chem. Commun.*, 2019, **106**, 95–98.

14 (*a*) D.-K. Cao, J.-S. Hu, M.-Q. Li, D.-P. Gong, X.-X. Li and M. D. Ward, *Dalton Trans.*, 2015, **44**, 21008–21015; (*b*) A. J. Hallett, B. D. Ward, B. M. Kariuki and S. J. A. Pope, *J. Organomet. Chem.*, 2010, **695**, 2401–2409; (*c*) A. F. Henwood, Y. Hu, M. T. Sajjad, G. K. V. V. Thalluri, S. S. Ghosh, D. B. Cordes, A. M. Z. Slawin, I. D. W. Samuel, N. Robertson and E. Zysman-Colman, *Chem. – Eur. J.*, 2015, **21**, 19128–19135; (*d*) L. Murphy, A. Congreve, L. O. Palsson and J. A. G. Williams, *Chem. Commun.*, 2010, **46**, 8743–8745; (*e*) S. A. Rommel, D. Sorsche, N. Rockstroh, F. W. Heinemann, J. Kübel, M. Wächtler, B. Dietzek and S. Rau, *Eur. J. Inorg. Chem.*, 2015, **2015**, 3730–3739.

15 L. He, Y. Li, C. P. Tan, R. R. Ye, M. H. Chen, J. J. Cao, L. N. Ji and Z. W. Mao, *Chem. Sci.*, 2015, **6**, 5409–5418.

16 (*a*) C.-K. Koo, Y.-M. Ho, C.-F. Chow, M. H.-W. Lam, T.-C. Lau and W.-Y. Wong, *Inorg. Chem.*, 2007, **46**, 3603–3612; (*b*) C. K. Koo, K. L. Wong, C. W. Y. Man, Y. W. Lam, L. K. Y. So, H. L. Tam, S. W. Tsao, K. W. Cheah, K. C. Lau, Y. Y. Yang, J. C. Chen and M. H. W. Lam, *Inorg. Chem.*, 2009, **48**, 872–878; (*c*) C.-K. Koo, K.-L. Wong, C. W.-Y. Man, H.-L. Tam, S.-W. Tsao, K.-W. Cheah and M. H.-W. Lam, *Inorg. Chem.*, 2009, **48**, 7501–7503.

17 T. Y. Lin, K. C. Tang, S. H. Yang, J. Y. Shen, Y. M. Cheng, H. A. Pan, Y. Chi and P. T. Chou, *J. Phys. Chem. A*, 2012, **116**, 4438–4444.

18 D. L. Davies, M. P. Lowe, K. S. Ryder, K. Singh and S. Singh, *Dalton Trans.*, 2011, **40**, 1028–1030.

19 N. M. Shavaleev, F. Monti, R. Scopelliti, N. Armaroli, M. Grätzel and M. K. Nazeeruddin, *Organometallics*, 2012, **31**, 6288–6296.

20 P. J. Spellane, R. J. Watts and C. J. Curtis, *Inorg. Chem.*, 1983, **22**, 4060–4062.

21 (*a*) W. Jiang, Y. Gao, Y. Sun, F. Ding, Y. Xu, Z. Bian, F. Li, J. Bian and C. Huang, *Inorg. Chem.*, 2010, **49**, 3252–3260; (*b*) F. Neve, M. La Deda, A. Crispini, A. Bellusci, F. Puntoriero and S. Campagna, *Organometallics*, 2004, **23**, 5856–5863; (*c*) E. Orselli, G. S. Kottas, A. E. Konradsson, P. Coppo, R. Fröhlich, L. De Cola, A. van Dijken, M. Büchel and H. Börner, *Inorg. Chem.*, 2007, **46**, 11082–11093; (*d*) Q. Zhao, S. Liu, M. Shi, C. Wang, M. Yu, L. Li, F. Li, T. Yi and C. Huang, *Inorg. Chem.*, 2006, **45**, 6152–6160.

22 (*a*) M. K. Nazeeruddin, R. T. Wegh, Z. Zhou, C. Klein, Q. Wang, F. De Angelis, S. Fantacci and M. Grätzel, *Inorg. Chem.*, 2006, **45**, 9245–9250; (*b*) M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal, G. G. Malliaras and S. Bernhard, *Chem. Mater.*, 2005, **17**, 5712–5719.

23 We have called the pK_a determined from the fluorescence titration the emission pK_a. The difference between this and the excited state pK_a is explained in J. G. Vos, *Polyhedron*, 1992, **11**, 2285–2299.

24 (*a*) W. S. Yu, C. C. Cheng, Y. M. Cheng, P. C. Wu, Y. H. Song, Y. Chi and P. T. Chou, *J. Am. Chem. Soc.*, 2003, **125**, 10800–10801; (*b*) X. Y. Yu, L. Deng, B. Zheng, B. R. Zeng, P. Yi and X. Xu, *Dalton Trans.*, 2014, **43**, 1524–1533.

25 M. Pichette Drapeau, T. Ollevier and M. Taillefer, *Chem. – Eur. J.*, 2014, **20**, 5231–5236.

26 C. Liu, X. Lv, Y. Xing and J. Qiu, *J. Mater. Chem. C*, 2015, **3**, 8010–8017.