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PAPER

Luminescent iridium complexes for detection of molybdate†

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Reactions of $[Ir(C^N)_2Cl]_2$ [HC^N = 2-(3-R-phenyl)pyridine, 2-(3-R-phenylpyrazole) R = H, Me] with Me_2-phencat give luminescent complexes $[Ir(C^N)_2(Me_2\text{-phencat})][PF_6]$ (**Me_2-2a, b, c**)$[PF_6]$. Deprotection of the methoxy groups with BBr_3 is problematic as simultaneous bromination of the cyclometallated phenyl groups occurs. However, deprotection of Me_2-phencat with BBr_3 followed by complexation with $[Ir(C^N)_2Cl]_2$ gives luminescent complexes $[Ir(C^N)_2(H_2\text{-phencat})][PF_6]$ (**H_2-3a, c**)$[PF_6]$, which are luminescent sensors for molybdate.

Introduction

Kinetically inert polypyridine complexes of metal ions with d^6 low-spin configuration, such as Ru(II), Re(I) and Ir(III), are increasingly used as signalling units in sensors and probes for biological targets, based on their high quantum yields, long excitation and emission wavelengths and reasonably long lifetimes.[1,2] In the field of anion recognition, metal-based luminophores of this type have shown promise in the development of sensors[3] for biologically important oxoanions, such as nitrate, sulfate, phosphate and phosphate derivatives.[2] Similarly, the detection of oxometalates of biological[4] and environmental[5] relevance, such as molybdate (MoO_4^{2-}), tungstate (WO_4^{2-}) and vanadate (HVO_4^{2-}), has recently attracted significant attention.[6]

In our previous work,[7] we have linked Ru(II)-and Re(I)-based luminophores to catecholamide-based receptor units that are able to distinguish biologically relevant oxometalates, such as MoO_4^{2-} or HVO_4^{2-}, from structurally related oxoanions, such as SO_4^{2-} or HPO_4^{2-}, as well as potentially competing cations, such as Cu^{2+} and Fe^{3+}. Upon binding to two catecholamide receptor units, the molybdenum centre increases its coordination number from four to six, as shown in Fig. 1. In the resulting distorted octahedral complex, the two strong oxo donors are positioned *cis* to each other, in order to maximise π-bonding.[8] As observed for 2, 3-dihydroxy benzoic acid,[9] a recently obtained crystal structure of the *cis*-dioxoMo(VI) complex of a catecholamides-based luminescent sensor revealed that the receptor unit, coordinates preferentially

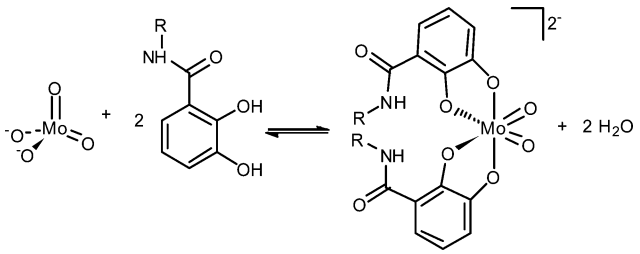

Fig. 1 The reaction of $[MoO_4]^-$ with catecholamides (R = signalling unit).

with the weaker donor in 2-position *trans* to the oxo-ligands to avoid competition for the same d-orbitals.[10]

Ru(II) and Re(I)-based signalling units respond to deprotonation or molybdate-binding to the receptor unit with a drastic decrease in emission intensity.[11] We are now interested to test whether catecholamide-linked Ir(III)-luminophores would respond similarly with a pH- and oxomatalate-dependent change in emission intensity.

Following the report by Thompson *et al.* in 1999[12] of an OLED, containing cyclometalated iridium complex $[Ir(ppy)_3]$ (Hppy = 2-phenylpyridine) as a dopant there has been a huge upsurge of interest in complexes $[Ir(C^N)_3]$ and $[Ir(C^N)_2(XY)]$. These complexes have high quantum yields for emission due to spin–orbit coupling and large Stokes shifts and as a result have been applied in luminescent sensors.[1,2] Early examples involved their use as oxygen sensors based on the quenching of emission by molecular oxygen.[13] Subsequently complexes with specific recognition sites appended to the ligands have been synthesised. Complexes $[Ir(C^N)_2(XY)]$ can be modified on the cyclometallating ligand or on the ancillary (XY) ligand. Huang *et al.* showed an aldehyde on a cyclometallated phenyl could react selectively with homocysteine causing a change in emission wavelength from 615 nm (red) to 525 nm (green), with a large enhancement in emission intensity.[14] Zhao *et al.* reported a complex $[Ir(C^N)_2(bipy)]^+$ containing bismesitylboryl groups on the cyclometallated phenyls, which is a highly selective chemosensor for fluoride ions detectable by the naked eye.[15] Alternatively, attaching the recognition site to the

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XY ligand has also been successful. Phenathroline and bipyridyl ligands have been functionalised with thioureas to sense anions[16] or with crown ethers or other ligands for metal ion sensing.[17]

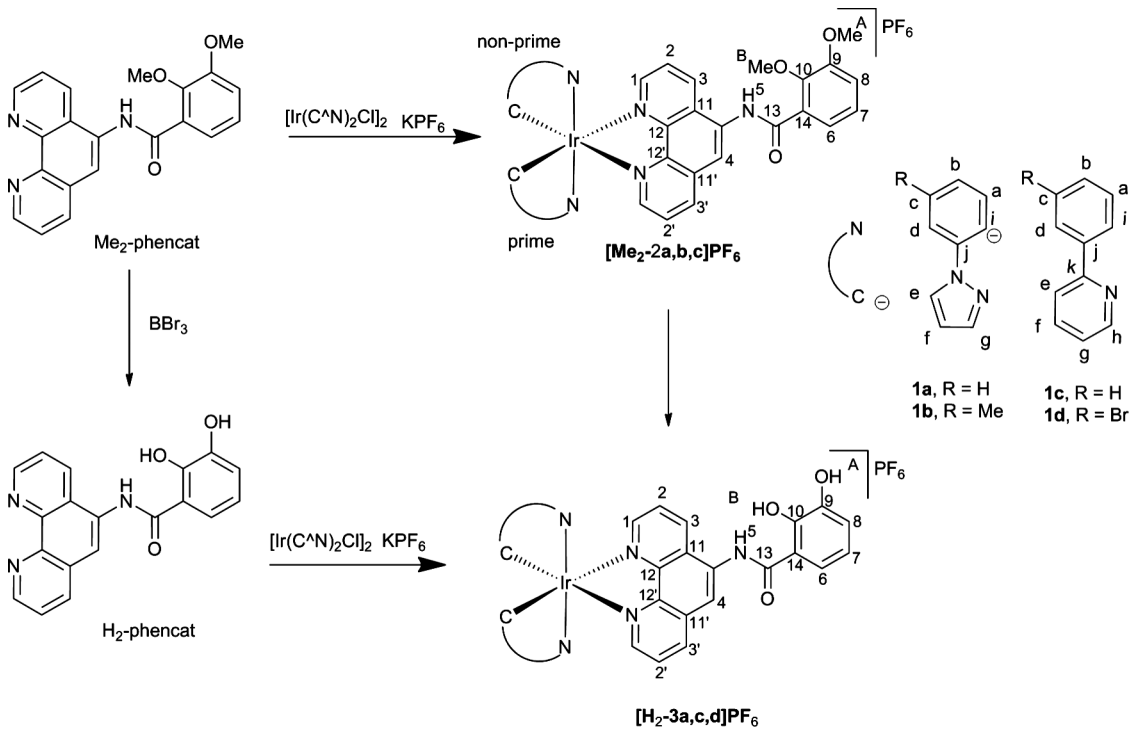
Lo *et al.* attached a biotin,[18] the complexes formed were non-emissive in aqueous buffer but enhanced emission intensities and extended lifetimes were observed upon binding to avidin. Given this range of sensing applications based on $[Ir(C^N)_2(XY)]$ complexes we decided to investigate their appplication for sensing molybdate based on a phenanthroline modified ligand we have designed previously.[7]

Results and discussion

The initial synthetic strategy was analogous to that used for the corresponding Ru(II) and Re(I) complexes[7] *i.e.* complexation of the protected ligand Me_2-phencat and then deprotection of methoxy groups using BBr_3 (Scheme 1). The ligand Me_2-phencat was prepared as reported earlier.[7] The dimers **1a,b,c** react with Me_2-phencat and KPF_6 at 60 °C under microwave irradiation for 20 min to form compounds **[Me_2-2a, b, c]**(PF_6) as yellow solids with yields of greater than 90% (Scheme 1).

The ^1H and ^{13}C NMR spectra of **[Me_2-2a, b, c]**(PF_6) are very complex due to the lack of C_2-symmetry and there is overlap of some signals in the aromatic region. For example, **[Me_2-2a]$^+$**, has in principle, 31 inequivalent protons, however, the ^1H NMR spectrum shows only seventeen different signals suggesting that there is substantial overlap. Nevertheless through the use of COSY, NOESY, TOCSY and HMQC measurements we have been able to assign the spectra. The most downfield signal in the ^1H NMR spectrum is a singlet at δ 10.84 assigned to the amide proton H_5 (confirmed by no cross peak in the HSQC ^1H–^{13}C) and is consistent with an intramolecular hydrogen bond between the amide N—H and the adjacent O atom of Me_2-phencat, as observed in the corresponding Ru(II)-and Re(I)-complexes.[7] The two OMe groups give rise to singlets at δ 3.98 and δ 4.11 assigned to Me_A and Me_B respectively due to NOEs to H_8 and H_5 respectively. H_4 is easily identified as the only other singlet at δ 9.02. The NOESY spectrum then allows identification of H_3 and $H_{3'}$ (NOE to H_5 and H_4 respectively) and the COSY spectrum assignment of $H_{1,1'}$ and $H_{2,2'}$. In the free ligand (Me_2-phencat), the signals for $H_{1,1'}$ are found at δ 9.16 and 9.04 respectively, but on co-ordination they shift to higher field (δ 8.53 and *ca.* 8.3, respectively) due to ring current effects from the neighbouring cyclometallated phenyls. H_1 shows an NOE to phenyl and pyrazole protons H_a and $H_{g'}$ respectively, similarly $H_{a'}$ and H_g both show NOEs to $H_{1'}$ which then allows assignment of all the other protons of the phenyl ($H_{a,a'-d,d'}$) and pyrazole ($H_{e,e'-g,g'}$) rings using the COSY spectrum. The protons $H_{a,a'}$ are observed as overlapping doublet of doublets at high field (δ 6.42 and δ 6.41 respectively) characteristic of the $[Ir(C^N)_2]$ fragment.[19] The phenyl protons give rise to only four signals integrating to two protons each, similarly the pyrazole groups are difficult to resolve. Presumably, the asymmetry of the Me_2-phencat ligand is too far away to make the phenylpyrazole ligands sufficiently different to resolve.

The ^1H NMR spectrum of **[Me_2-2b]$^+$** is similar to that of **[Me_2-2a]$^+$** except in **[Me_2-2b]$^+$** one proton on each phenyl has been replaced by a methyl ($Me_{C,C'}$), which are observed as coincident singlets at δ 2.34. The most downfield singlet signals, at δ 10.82 and δ 9.03 are assigned to H_5 and H_4 respectively. The orientation of the amide is the same as **[Me_2-2a]$^+$** as evidenced by the NOE between the NH, and one of the OMe groups (Me_B) at δ 4.11 and the short N—H···O distance observed in the crystal structure (see below). The ^1H NMR spectrum of **[Me_2-2c]$^+$** is also similar to **[Me_2-2a]$^+$** with the amide proton H_5 being observed at δ 10.81. The



Scheme 1 Synthesis of complexes **[Me_2-2a, b, c]** and **[H_2-3a, c, d]** with labelling for NMR assignments.

pyridine protons $H_{h,h'}$ observed at 9.25 in the starting dimer[20] are shifted to δ 8.06 due to the ring current effect of the coordinated phencat-OMe ligand. The FAB mass spectra show molecular ions for the cations at *m/z* 838, 866, 860 for **[Me$_2$-2a, b, c]$^+$** respectively. All three complexes gave satisfactory microanalyses.

Single crystals of **[Me$_2$-2b]**(PF_6) were obtained by slow diffusion of hexane into a concentrated DCM solution of the salt. The crystal structure is shown in Fig. 2, with selected bond lengths (Å) and angles (°). The Ir(III) has a distorted octahedral coordination geometry [N(1)–Ir(1)–N(3) is 171.32°], with *cis* metallated carbons and *trans* nitrogen atoms, as expected for such systems.[21] The catechol unit is held planar by an intramolecular hydrogen bond N–H···O (d(N–O) = 2.680 Å) as discussed above and as observed in similar Re(I) and Ru(II) complexes (d(N–O) = 2.649 Å and 2.641 Å respectively).[7]

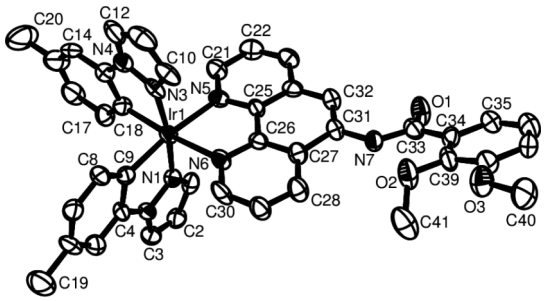


Fig. 2 X-ray crystal structure of the cation of **[Me$_2$-2b]** with selected bond lengths (Å) and bond angles (°): Ir(1)–N(1), 2.007(5); Ir(1)–N(3), 1.997(5); Ir(1)–N(5), 2.128(4); Ir(1)–N(6), 2.124(4); Ir(1)–C(9), 2.005(6); Ir(1)–C(18), 2.009(6); N(1)–Ir(1)–N(3), 171.32(19); N(1)–Ir(1)–C(9), 80.4(2); N(3)–Ir(1)–C(18), 80.1(2); N(5)–Ir(1)–N(6), 77.07(18).

In order to bind molybdate the methoxy groups need to be deprotected to provide the catechol. This was attempted using BBr_3 following the literature method.[7] In the first attempt this led cleanly to a new complex which showed a mass approximately 160 units higher than expected. The ^{1}H NMR spectra of the product showed no signals for OMe groups showing that the deprotection had been successful. In addition there were only three signals for each cyclometallated phenyl, doublets for $H_{a/a'}$ and $H_{d/d'}$ and doublet of doublets for $H_{b/b'}$ consistent with bromination on both phenyl rings *para* to the metal. The other signals were similar to **[Me$_2$-2c]$^+$** hence the product was identified as **[H$_2$-3d]$^+$**. Note, a direct bromination of the phenyl ring at the *para* positon with respect to the metal in $[Ir(ppy)_2Cl]_2$ has been reported using pyridinium tribromide.[22] The ^{13}C–{^{1}H} NMR spectra of **[H$_2$-3d]$^+$** show the expected signals though there is some overlap between signals of related groups. The FAB mass spectrum shows an ion at *m/z* 990 with the appropriate isotope pattern due to **[H$_2$-3d]$^+$** and the microanalysis is satisfactory, confirming the dibromination.

In an attempt to prevent bromination of the phenyl complex, **[Me$_2$-2c]**(PF_6) was reacted with a 10-fold molar excess of BBr_3 in DCM at −78 °C. Monitoring by ES-MS showed that deprotection of the first methyl occurred within one hour, but deprotection of the second methyl was much slower requiring several days at room temperature (RT) and a large excess of BBr_3 to go to completion, which suggests one OMe is perhaps less basic than the other as found previously.[7] Unfortunately, bromination of one of the cyclometallated phenyls is competitive with the second deprotection as evidenced by peaks *ca* 80 Daltons higher showing a correct isotope pattern for substitution of one hydrogen by bromine. Unfortunately, it was not possible to separate out a pure component from these mixtures. If the reaction was left for a long time, and additional BBr_3 added as necessary, conversion to the dibrominated product **[H$_2$-3d]$^+$** was possible. Iodotrimethylsilane was also tried instead of BBr_3 as a deprotecting reagent for **[Me$_2$-2c]**(PF_6), however this only gave the mono deprotected product as judged by ES-MS. Corresponding reactions of BBr_3 with **[Me$_2$-2a]**(PF_6) and **[Me$_2$-2b]**(PF_6) also gave inseparable mixtures of products with bromination being evident in the ES-MS for both of the complexes. For **[Me$_2$-2b]**(PF_6) bromination cannot occur on the position *para* to the metal; however, the actual site of bromination could not be identified, as the ^{1}H NMR spectrum showed very broad peaks.

Since deprotection of the complexed ligand was complicated by simultaneous bromination of the cyclometallated phenyl(s), the alternative approach of deprotecting the ligand and then complexation to the metal was attempted. The ligand Me_2-phencat was deprotected using BBr_3 however, the product is insoluble in organic solvents and in water, hence it was purified by washing successively with MeOH, DCM and diethylether. A ^{1}H NMR spectrum could be obtained in D_2O in the presence of NaOD, however the spectrum showed some evidence of exchange processes occurring and the solution decomposed over time hence the spectrum was not fully assigned. However, even though the ligand is not soluble it is able to react with the iridium dimers **1a** and **1c** under microwave irradiation. to give the expected products **[H$_2$-3a]**(PF_6) and **[H$_2$-3c]**(PF_6) respectively in high yields (~ 80%) (Scheme 1).

The ^{1}H and ^{13}C NMR spectra of **[H$_2$-3a]$^+$** and **[H$_2$-3c]$^+$** are similar to those of **[Me$_2$-2a]$^+$** and **[Me$_2$-2c]$^+$** respectively, except the signals due to the phencat-ligands. The amide proton H_5 is not observed for either complex, probably due to exchange with the solvent (MeOD). The only singlet is therefore assigned to H_4 (δ 8.81 and 8.87 for **[H$_2$-3a]$^+$** and **[H$_2$-3c]$^+$** respectively) which shows an NOE to $H_{3'}$. The catechol protons H_{6-8} are identified using the HMBC spectra as proton H_6 shows a cross peak to C_{10} and proton H_7 shows a cross peak to C_9 respectively in each case. The other assignments are made on the same basis as for **[Me$_2$-2a]$^+$**, in some cases the protons of the cyclometallated ligands ($H_{a-g/h}$ and $H_{a'-g'/h'}$) are accidentally equivalent. Protons $H_{a,a'}$ are again at high field and show NOEs to H_1 and $H_{1'}$ respectively. The ^{13}C–{^{1}H} NMR spectra show the expected signals and the FAB mass spectra show peaks for ions at *m/z* 810 and 832 for **[H$_2$-3a]$^+$** and **[H$_2$-3c]$^+$**, respectively.

Photophysical measurements

Selected spectroscopic characteristics for complexes **[Me$_2$-2]$^+$** and **3** are shown in Table 1. Due to the limited water solubility of the complexes, to examine the effect of pH on absorption a mixed solvent system consisting of acetonitrile and water (20 : 1) was used. The absorption spectra of the protected complexes **[Me$_2$-2a]$^+$** and **[Me$_2$-2c]$^+$** are pH independent (between pH 0.1 and 11), but those of the deprotected ones **[H$_2$-3a, c, d]$^+$** show an increase in intensity with increase in pH due to deprotonation and formation of **[H-3a, c, d]**, as shown for **[H$_2$-3a]$^+$** in Fig. 3. and **[H$_2$-3c]$^+$** and **[H$_2$-3d]$^+$** in the supporting information.

Table 1 Selected spectroscopic data and protonation constants for **[Me$_2$-2a]$^+$** and **[Me$_2$-2c]$^+$** and the protonated and mono-deprotonated forms of **3a**, **3c** and **3d** (aerated solutions at room temperature in aqueous acetonitrile (5% water))

	[Me$_2$-2a]$^+$	**[Me$_2$-2c]$^+$**	**[H$_2$-3a]$^+$**	**[H-3a]**	**[H$_2$-3c]$^+$**	**[H-3c]**	**[H$_2$-3d]$^+$**	**[H-3d]**
Absorption λmax/nm	325	378	319	326	329, 375 sh	334 sh, 374 sh	375 sh, 420 sh	400 sh
Emission λem/nm (λex/nm)	596	609	596	—	610	—	588	—
	(325)	(330)	(326)	(326)	(330)	(330)	(400)	(400)
Excitation λex/nm (λem/nm)	325	340	280, 326	—	285, 330	314	375	—
	(600)	(609)	(596)	(596)	(610)	(610)	(588)	(588)
pK_a	—	—	5.6		5.6		5.7	
pHi[a]	—	—	6.0		6.0		5.6	

sh = shoulder[a] pHi is the pH at the inflection point of the fluorescence titration curve.

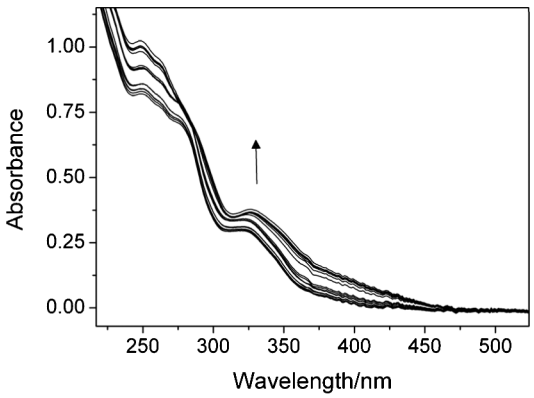


Fig. 3 Absorption spectra recorded between pH 1.0 and 10.6 during the titration of an acidic solution (0.015 mM) of **[H$_2$-3a]$^+$** in aqueous acetonitrile (5% water) with [Me$_4$N]OH.

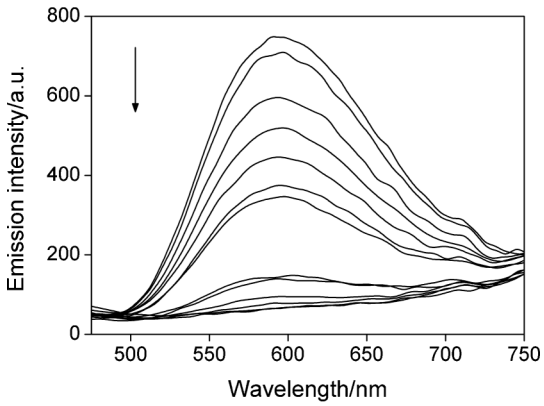


Fig. 4 Emission spectra recorded between pH 1.0 and 10.6 during the titration of an acidic solution (0.015 mM) of **[H$_2$-3a]$^+$** in aqueous acetonitrile (5% water) with [Me$_4$N]OH.

The absorption spectra of 2, 3-dihydroxybenzamides generally show an increase in the intensity of the lowest energy absorbance band upon deprotonation of the *ortho* OH group of the catecholamide unit[10,23] hence, the increase in absorbance of **[H$_2$-3a, c, d]$^+$** with pH is attributed to the deprotonation of the *ortho*-OH group on the catechol unit of the phencat ligand. This is consistent with the Ru(II) and Re(I) complexes of the same ligand.[7] From the pH profiles obtained, pK_a-values of 5.6, 5.6 and 5.7 can be estimated for **[H$_2$-3a]$^+$**, **[H$_2$-3c]$^+$** and **[H$_2$-3d]$^+$**, respectively (Table 1). Consequently, the change of the ancillary ligand from **1a** to **1c** and **1d** has no significant effect on the pK_a value of the phencat receptor unit.

Upon excitation both the protected and deprotected complexes **2** and **3**, respectively, show emission in acetonitrile and the data are tabulated in Tables 1. The emission of complex **[H$_2$-2a]$^+$** is solvent sensitive, a red shift (10 nm) is observed upon increasing the polarity of the solvent from DCM to acetonitrile/MeOH, which is consistent with a charge transfer component in the emissive state. Each of the deprotected complexes **[H$_2$-3a, c, d]$^+$** also show a red shift (10–20 nm) in emission upon changing the solvent from acetonitrile to a mixture of acetonitrile:water (20 : 1). In aqueous acetonitrile, complexes **[H$_2$-3a, c, d]$^+$** show long wavelength emission bands with maxima at 596, 610 and 588 nm, respectively. For complex **[H$_2$-3d]$^+$** the emission is higher energy than for **[H$_2$-3c]$^+$** consistent with an electron withdrawing substituent (Br) on the cyclometalated phenyl *para* to the metal.[24] The intensity of the emission decreases sigmoidally with increasing pH for each complex (as shown for **[H$_2$-3a]$^+$** in Fig. 4 and for **[H$_2$-3c]$^+$[H$_2$-3d]$^+$** in the supporting information†) which is attributed to the deprotonation of the catechol unit, giving **[H-3a, c, d]**.

This assertion is further supported by the observation that the emission intensity of the protected complexes **[Me$_2$-2a, c]$^+$** is pH independent. In addition, emission quenching upon deprotonation of phenolic OH groups has been reported for similar systems.[25] From the inflection points of the pH-profiles obtained for **[H$_2$-3a]$^+$**, **[H$_2$-3c]$^+$** and **[H$_2$-3d]$^+$**, pH$_i$ values of 6.0, 6.0 and 5.6, respectively, were estimated (Table 1), again indicating that the ancillary ligand has only little influence on the donor strength of the phencat ligand.

The addition of 0.5 equivalents of molybdate to solutions of the deprotected complexes **[H$_2$-3a, c, d]$^+$** results in a decrease of the emission intensity in the acidic pH range. The emission intensity at 596 for **[H$_2$-3a]$^+$** at various pH is shown in Fig. 5 (for **[H$_2$-3c, d]$^+$** see supporting information†). As expected from previous studies with Re(I) and Ru(II) complexes the decrease in emission intensity of the complexes **[H$_2$-3a, c, d]$^+$** is proportional to the concentration of molybdate, due to deprotonation of the catechol units upon metal-ion coordination. The observation that the emission intensity of the methyl protected complexes **[Me$_2$-2a]$^+$** and **[Me$_2$-2c]$^+$** is not influenced by the presence of molybdate supports this assertion and demonstrates that the decrease in emission intensity is not due to intermolecular quenching processes.

To determine the composition of the Mo complexes formed, the solutions of **[H$_2$-3a, c, d]$^+$** were titrated with aqueous solutions

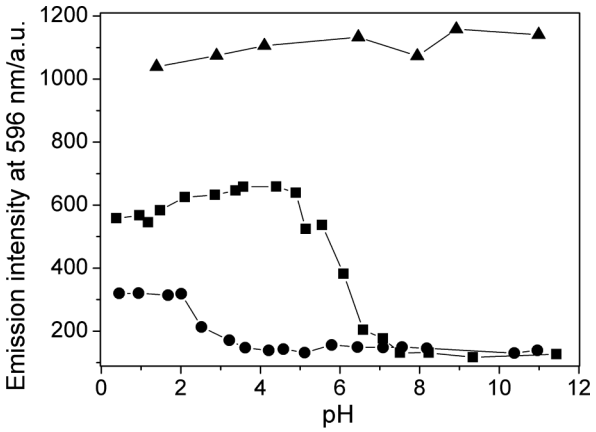


Fig. 5 Emission intensity at 596 nm as a function of pH recorded for **[Me$_2$-2a]** (triangles), **[H$_2$-3a]$^+$** (squares) and **[H$_2$-3a]$^+$** + 0.5 equiv. molybdate (circles) upon titration of acidic 0.015 mM solutions with [Me$_4$N]OH (aqueous acetonitrile, 5% water).

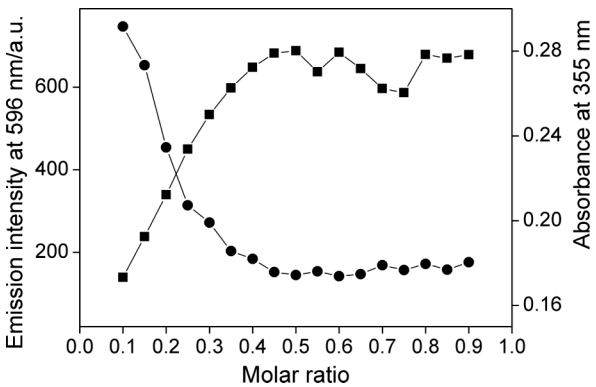
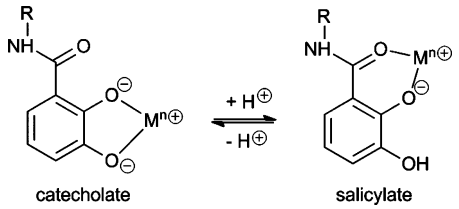


Fig. 6 Emission intensity at 596 nm and absorbance at 355 nm of a 0.02 mM solution of **[H$_2$-3a]$^+$** in aqueous acetonitrile at pH 4.1 as a function of molar MoO_4^{2-} fractions.

of molybdate, as shown for **[H$_2$-3a]$^+$** in Fig. 6 (for **[H$_2$-3c, d]$^+$** see supporting information†). During the titrations, the solutions were buffered at pH values 4.1, 4.7 and 4.1 for **[H$_2$-3a, c, d]$^+$**, respectively. Upon the addition of molybdate the emission intensity of all the three sensors decreases almost linearly until a ratio of sensor to molybdate of approximately 2 : 1 is reached. This ratio is consistent with the predominant formation of *cis*-dioxo-Mo(VI)-dicatecholate complexes at these pH values. Complexes of this composition are well known in the literature.[9,10,26]

Below pH 4, protonation of the Mo-complex is observed, which leads to an increase in emission intensity. The most likely first protonation site is the basic OH-group in *meta*-position of the catecholamide unit. Such protonation can give rise to a change in the co-ordination mode of the catecholamide unit, which can facilitate dissociation. For Fe(III)-catecholamide complexes, it is known that coordination to the carbonyl oxygen rather than the basic phenolate in *meta*-position becomes more favourable as the pH is lowered (salicylate mode of binding, Scheme 2). We have previously investigated the Mo-complex of a Ru-based sensor that contains the same catecholamide receptor unit as **[H3-3a,c,d]$^+$** in more detail at pH 4.0.[27] For the Ru-based sensor, we were able to confirm that a change in binding mode rather than complete catecholamide dissociation is the predominant mechanism at this



Scheme 2 Alternate binding mode for monodeprotonated ligand.

pH. A shift to the salicylate mode of binding is conceivable since *cis*-dioxo Mo(VI) salicylate complexes, such as $[MoO_2(sal)_2]^{2-}$ ($salH_2$ = salicylic acid), are documented in the literature.[28] Since protonation and shift to the salicylate mode of binding decreases the stability of the Mo-complex, partial dissociation takes place below pH 4 and the presence of the released **[H$_2$-3a]$^+$** leads to an increase in emission intensity.

Conclusions

We have shown that bis-cyclometallated iridium complexes can be used as luminescent reporters of changes in pH or molybdate concentration using our previously described catecholamide receptor for molybdate. Further fine tuning of the ligand environment around iridium is needed to improve the response beyond ruthenium analogues. Notably the synthesis of these complexes, differs from the previous ruthenium and rhenium complexes. In the case of iridium the deprotection of the catechol has to be done before complexation to the metal due to competing bromination of the cyclometallated phenyl groups by BBr_3. The reactivity of the cyclometallated phenyls towards electrophilic reagents may be a general problem for other ligand modifications carried out after complexation.

Experimental

Unless stated otherwise all reactions were carried out under an inert atmosphere of nitrogen and under microwave irradiation. After work up all the complexes were stable in air. Microwave reactions were carried out in a *CEM-Discover* commercial microwave reactor. ^{1}H, and ^{13}C–{^{1}H} NMR spectra were obtained using a DRX 400 MHz spectrometer. Chemical shifts were recorded in ppm (on δ scale with tetramethylsilane as internal reference), and coupling constants are reported in Hz. FAB mass spectra were obtained on a Kratos concept mass spectrometer using NOBA as matrix. The electrospray (ES) mass spectra were recorded using a micromass Quattra LC mass spectrometer in HPLC grade acetonitrile. Microanalyses were performed by the Elemental Analysis Service (London Metropolitan University). Emission and excitation spectra were recorded on a Hitachi F-4500 fluorimeter, equipped with a red-sensitive R928F photomultiplier tube. All starting materials were obtained from Aldrich or Alfa Aesar with the exception of dimers **1a–c**[24] and Me$_2$-phencat[7] ligand which were prepared according to literature methods.

Preparation of [Me$_2$-2a](PF$_6$)

Dimer **1a** (70 mg, 0.068 mmol), Me$_2$-phencat (59 mg, 0.164 mmol) and KPF_6 (25 mg, 0.136 mmol) were placed in a microwave vial

and methanol (3 ml) was added. Nitrogen was bubbled through the solution for 2 min and the vial was then sealed with a septum cap. The reaction mixture was then heated under microwave irradiation for 20 min at 60 °C. 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 volume of the filtrate was reduced and hexane was added slowly to induce precipitation. The precipitate was filtered, washed with hexane and dried *in vacuo* to yield **[Me$_2$-2a]**(PF$_6$) as a yellow solid (121 mg, 91%). Anal. Calcd for $C_{39}H_{31}N_7O_3IrPF_6$: C, 47.66, H, 3.18, N, 9.98. Found: C, 47.76, H, 3.24, N, 9.92%. ^{1}H NMR (CD_3CN): δ 10.84 (1H, s, H_5), 9.02 (1H, s, H_4), 8.77 (1H, dd, J = 8.6, 1.2, H_3), 8.69 (1H, dd, J = 8.6, 1.6, $H_{3'}$), 8.53 (1H, dd, J = 5.1, 1.2, H_1), 8.38–8.37 (3H, m, $H_{1',e,e'}$), 7.96 (1H, dd, J = 8.2, 5.1, H_2), 7.82 (1H, dd, J = 8.2, 5.1, $H_{2'}$), 7.73 (1H, dd, J = 7.1, 2.7, H_6), 7.53 (2H, d, J = 8.2, $H_{d,d'}$), 7.36–7.30 (2H, m, $H_{7,8}$), 7.13 (2H, tt, J = 7.4, 1.2, $H_{c,c'}$), 6.97–6.92 (4H, m, $H_{b,b',g,g'}$), 6.51, 6.50 (2H, 2 × t, J = 2.7, $H_{f,f'}$), 6.42, 6.41 (2H, 2 × dd, J = 7.4, 0.8, $H_{a,a'}$), 4.11 (3H, s, Me_B), 3.98 (3H, s, Me_A). ^{13}C NMR: 164.48 (C_{13}), 152.94 (C_9), 151.75 (C_1), 150.46 ($C_{1'}$), 147.97 (C_{12}), 147.56 (C_{10}), 145.22 ($C_{12'}$), 143.45, 143.38 ($C_{h,h'}$), 138.85 ($C_{g,g'}$), 138.13 ($C_{3'}$), 134.04 (C_{11}), 133.24, 133.19 ($C_{a,a'}$), 132.98 (C_3), 131.85, 131.52, 131.30 ($C_{11',14,i,i'}$), 127.91 ($C_{e,e'}$), 126.78 ($C_{2'}$), 126.53 ($C_{b,b'}$), 126.32 (C_2), 124.82 (C_7), 123.36 ($C_{c,c'}$) 122.08 (C_6), 117.99 (C_4), 116.80 (C_8), 111.96 ($C_{d,d'}$), 108.05 ($C_{f,f'}$), 61.57 (Me_B), 55.91 (Me_A). MS (FAB): m/z 838 [M]$^+$.

Preparation of [Me$_2$-2b](PF$_6$)

The procedure was the same as for **[Me$_2$-2a]**(PF$_6$) using dimer **1b** (100 mg, 0.092 mmol), Me$_2$-phencat (79.3 mg, 0.221 mmol) and KPF_6 (40.7 mg, 0.221 mmol), and after work up gave **[Me$_2$-2b]**(PF$_6$) as a yellow solid (154 mg, 83%). Anal. Calcd for $C_{41}H_{35}N_7O_3IrPF_6$: C, 48.71, H, 3.49, N, 9.70. Found: C, 48.80, H, 3.57, N, 9.65%. ^{1}H NMR (400 MHz, CD_3CN): δ 10.82 (1H, s, H_5), 9.03 (1H, s, H_4), 8.77 (1H, dd, J = 8.6, 1.2, H_3), 8.69 (1H, dd, J = 8.6, 1.6, $H_{3'}$), 8.56 (1H, dd, J = 5.1, 1.2, H_1), 8.40 (1H, dd, J = 5.1, 1.2, $H_{1'}$), 8.34, 8.33 (2H, 2 × d, J = 2.7, $H_{e,e'}$), 7.97 (1H, dd, J = 8.6, 5.1, H_2), 7.83 (1H, dd, J = 8.2, 5.1, $H_{2'}$), 7.74 (1H, dd, J = 7.0, 2.7, H_6), 7.39 (2H, s, $H_{d,d'}$), 7.36–7.30 (2H, m, $H_{7,8}$), 6.89, 6.88 (2H, 2 × d, J = 2.7, $H_{g,g'}$), 6.79 (2H, bd, J = 7.4, $H_{b,b'}$), 6.49, 6.48 (2H, 2 × t, J = 2.7, $H_{f,f'}$), 6.26, 6.25 (2H, 2 × d, J = 7.4, $H_{a,a'}$), 4.11 (3H, s, Me_B), 3.98 (3H, s, Me_A), 2.34 (6H, s, $Me_{C,C'}$). ^{13}C NMR: 165.50 (C_{13}), 154.02 (C_9), 152.82 (C_1), 151.53 ($C_{1'}$), 149.10 (C_{12}), 148.65 (C_{10}), 146.36 ($C_{12'}$), 144.52, 144.45 ($C_{h,h'}$), 139.76 ($C_{g,g'}$), 139.12 ($C_{3'}$), 135.05 ($C_{c,c'}$), 134.02 ($C_{a,a'}$), 133.97 (C_{14}), 133.89 (C_3), 132.35 ($C_{11'}$), 128.66 ($C_{b,b'}$), 128.42 ($C_{e,e'}$), 128.34 ($C_{i,i'}$), 127.81 (C_{11}), 127.61 ($C_{2'}$) 127.39 (C_2), 125.93 (C_7), 123.18 (C_6), 119.03 (C_4), 117.92 (C_8), 113.76 ($C_{d,d'}$), 109.02 ($C_{f,f'}$) 62.66 (Me_B), 56.99 (Me_A), 21.11 ($Me_{C,C'}$). MS (FAB): m/z 866 [M]$^+$.

Preparation of [Me$_2$-2c](PF$_6$)

The procedure was of the same as for **[Me$_2$-2a]**(PF$_6$) using dimer **1c** (70 mg, 0.065 mmol), Me$_2$-phencat (56.1 mg, 0.156 mmol) and KPF_6 (26.4 mg, 0.144 mmol), and after work up gave **[Me$_2$-2c]**(PF$_6$) as a yellow solid (119 mg, 91%). Anal. Calcd for $C_{43}H_{33}N_5O_3IrPF_6$: C, 51.39, H, 3.31, N, 6.97. Found: C, 51.41, H, 3.26, N, 6.94%. ^{1}H NMR (CD_3CN): δ 10.81 (1H, s, H_5), 9.03 (1H, s, H_4), 8.74 (1H, dd, J = 8.6, 1.4, H_3), 8.65 (1H, dd, J = 8.4, 1.4, $H_{3'}$), 8.37 (1H, dd, J = 5.2, 1.4, H_1), 8.22 (1H, dd, J = 5.2, 1.4, $H_{1'}$), 8.06 (2H, m, $H_{h,h'}$), 7.94 (1H, dd, J = 8.6, 5.2, H_2), 7.84 (2H, dd, J = 7.7, 1.0, $H_{d,d'}$), 7.82–7.76 (3H, m, $H_{2',g,g'}$), 7.71 (1H, dd, J = 6.9, 2.6, H_6), 7.45 (2H, ddd, J = 5.8, 2.1, 1.4, $H_{e,e'}$), 7.33–7.27 (2H, m, $H_{7,8}$), 7.09, 7.08 (2H, 2 × td, J = 7.6, 1.4, $H_{c,c'}$), 6.97, 6.96 (2H, 2 × td, J = 7.4, 1.4, $H_{b,b'}$), 6.88, 6.87 (2H, 2 × td, J = 7.2, 1.2, $H_{f,f'}$), 6.40, 6.39 (2H, 2 × dd, J = 7.6, 0.8, $H_{a,a'}$) 4.07 (1H, s, Me_B) 3.95 (1H, s, Me_A). ^{13}C NMR: 167.52, 167.47 ($C_{k,k'}$), 164.44 (C_{13}), 152.95 (C_9), 151.44 (C_1), 150.16 ($C_{1'}$), 150.02 ($C_{i,i'}$), 149.68 (C_{14}), 149.41 ($C_{e,e'}$), 147.59 (C_{10}), 147.33 (C_{12}), 144.53 ($C_{11'}$), 144.33 (C_{12}), 144.27 ($C_{j,j'}$), 138.49 ($C_{g,g'}$), 138.07 ($C_{3'}$), 134.16 (C_{11}), 132.82 (C_3), 131.75, 131.70 ($C_{a,a'}$), 130.37 ($C_{b,b'}$), 127.00 ($C_{2'}$) 126.79 (C_2), 124.87 ($C_{7,d,d'}$), 123.40, 123.36 ($C_{f,f'}$), 122.66 ($C_{c,c'}$), 122.12 (C_6), 119.82 ($C_{h,h'}$), 118.12 (C_4) 116.88 (C_8), 61.59 (Me_B), 55.93 (Me_A). MS (FAB): m/z 860 [M]$^+$.

Attempted deprotection of [Me$_2$-2c](PF$_6$)

Under an inert atmosphere, **[Me$_2$-2c]**(PF$_6$) (100 mg, 0.099 mmol) was dissolved in dry DCM (8 ml). The solution was cooled to −78 °C and a 10-fold molar excess (per methoxy) of 1.0 M BBr_3 in DCM was added slowly. The reaction was stirred at −78 °C for 1 h and then allowed to warm to room temperature. The reaction was then stirred at room temperature for a further 14 days and a total of 28 equiv (per methoxy) of 1.0 M BBr_3 in DCM was added at different time intervals. The reaction was monitored *via* ^{1}H NMR spectroscopy and ES mass spectrometry. Molecular ions were observed at m/z 846, 832, corresponding to the monodeprotected complex, and di-deprotected cation **[H$_2$-3c]**$^+$, along with ions at m/z 924, 910, 1004 and 990 (*i.e.* approximately 80 and 160 mass units higher) the isotope patterns of which were consistent with containing one or two bromine atoms respectively. After 14 days only m/z 990 was observed so the reaction was worked up by slow addition of water until no HBr was evolved. The reaction mixture was evaporated to dryness and the residues were taken up in methanol. KPF_6 (32.2 mg, 0.175 mmol) was added the mixture was stirred for 30 min. and was then evaporated to dryness and the solid was dissolved in DCM (20 ml) and passed through celite. The volume of the filtrate was reduced and hexane was added slowly to induce precipitation. The precipitate was isolated, washed with hexane and dried *in vacuo* to yield **[H$_2$-3d]**(PF$_6$) as a yellow solid (79 mg, 75%). Anal. Calcd for $C_{41}H_{27}N_5O_3Br_2IrPF_6$: C, 43.40, H, 2.40, N, 6.17. Found: C, 43.32, H, 2.39, N, 6.14%. ^{1}H NMR (400 MHz, CD_3CN): δ 10.59 (1H, s, H_5), 8.84 (1H, dd, J = 8.6, 1.6, H_3), 8.67 (1H, dd, J = 8.6, 1.6, $H_{3'}$), 8.67 (1H, s, H_4), 8.37 (1H, dd, J = 5.1, 1.6, H_1), 8.27 (1H, dd, J = 5.1, 1.2, $H_{1'}$), 8.08, (2H, bd, J = 8.2, $H_{e,e'}$), 8.01 (2H, d, J = 1.9, $H_{d,d'}$), 7.87 (1H, dd, J = 8.6, 5.1, H_2), 7.84–7.78 (4H, m, $H_{2',6,f,f'}$), 7.46 (2H, m, $H_{h,h'}$), 7.17 (1H, dd, J = 7.8, 1.6, H_8), 7.11, 7.10 (2H, 2 × dd, J = 8.2, 1.9, $H_{b,b'}$), 6.95–6.91 (3H, m, $H_{7,g,g'}$), 6.27, 6.26 (2H, 2 × d, J = 8.2, $H_{a,a'}$). ^{13}C NMR: 169.67 (C_{13}), 166.89, 166.81 ($C_{k,k'}$), 152.77 (C_1), 151.85 ($C_{1'}$), 150.84, 150.76 ($C_{h,h'}$), 149.02 ($C_{i,i'}$), 148.73 (C_{10}), 148.20 (C_{12}), 147.91, 147.85 ($C_{j,j'}$), 146.87 (C_9), 146.13 ($C_{12'}$), 139.89 ($C_{f,f'}$), 139.50 ($C_{3'}$), 135.81 (C_3), 134.91 (C_{12}), 134.59, 134.56 ($C_{a,a'}$), 133.76 ($C_{b,b'}$), 132.29 ($C_{11'}$), 129.23 (C_{11}), 128.59, 128.56 ($C_{d,d'}$) 128.10 ($C_{2'}$), 127.58 (C_2), 125.32 ($C_{g,g'}$), 122.82 (C_4), 121.52, 121.47 ($C_{e,e'}$), 120.99 (C_7), 120.91 (C_8) 120.56 (C_6), 117.40 (C_{14}), 117.05 ($C_{c,c'}$). MS (FAB): m/z 990 [M]$^+$.

Preparation of H_2-phencat

An excess of BBr_3 (8.4 mmol of 1.0 M solution in CH_2Cl_2) was added to Me_2-phencat (150 mg, 0.43 mmol) in CH_2Cl_2 (5 ml) at −78 C and left to stir overnight. After 24 h H_2O was added slowly until no more HBr evolved. Volatile impurities were removed by addition of methanol (3 × 10 ml) followed by rotary evaporation. The residual solid was washed with methanol CH_2Cl_2 and ether. The resulting solid was insoluble in common organic solvents and water however an ^{1}H NMR spectrum could be run in D_2O/NaOD: δ 8.85 (1H, d, J = 3.5, phen), 8.73 (1H, br s, phen), 8.57 (1H, d, J = 8.5, phen), 8.07 (2H, s, phen), 7.67 (1H, dd, J = 4, 8.5, phen), 7.48 (1H, br s, phen), 7.25 (1H, dd, J = 2, 8, cat), 6.85 (1H, dd, J = 1.5, 7.5, cat), 6.57 (1H, t, J = 7.5, cat). ES-MS m/z 332 $[M+H]^+$.

Preparation of [H_2-3a](PF_6)

A mixture of dimer **1a** (70 mg, 0.068 mmol) and H_2-phencat (72.8 mg, 0.176 mmol) in methanol (2 ml) was degassed and heated under microwave irradiation for 2 h. at 70 °C. The orange-yellow solution was then cooled to room temperature and KPF_6 (32.3 mg, 0.176 mmol) was added to the solution and stirred for 30 min. The mixture was evaporated to dryness and the solid was dissolved in DCM (15 ml) and passed through celite. The volume of the filtrate was reduced and hexane was added slowly to induce precipitation. The precipitate was filtered, washed with hexane and dried *in vacuo* to yield **[H_2-3a]**(PF_6) as a yellow solid (101 mg, 78%). Anal. Calcd for $C_{37}H_{27}N_7O_3IrPF_6$: C, 46.54, H, 2.85, N, 10.27. Found: C, 46.63, H, 2.76, N, 10.27%. ^{1}H NMR (400 MHz, MeOD): δ 8.87 (1H, dd, J = 8.6, 1.2, H_3), 8.81 (1H, s, H_4), 8.69 (1H, dd, J = 8.6, 1.2, $H_{3'}$), 8.55–8.53 (3H, m, $H_{1, e, e'}$), 8.43 (1H, dd, J = 5.1, 1.6, $H_{1'}$), 7.94 (1H, dd, J = 8.6, 5.1, H_2), 7.86 (1H, dd, J = 8.6, 5.1, $H_{2'}$), 7.60 (1H, dd, J = 8.2, 1.2, H_6), 7.55 (2H, bd, J = 7.8, $H_{d, d'}$), 7.12–7.05 (3H, m, $H_{8, c, c'}$), 6.96, 6.95 (2H, 2 × d, J = 2.3, $H_{g, g'}$), 6.91, 6.90 (2H, 2 × td, J = 7.4, 0.8, $H_{b, b'}$), 6.87 (1H, t, J = 8.2, H_7), 6.53, 6.52 (2H, 2 × d, J = 2.3, $H_{f, f'}$), 6.42, 6.41 (2H, 2 × dd, J = 7.4, 1.2, $H_{a, a'}$). ^{13}C NMR: 167.78 (C_{13}), 151.32 (C_1), 150.38 ($C_{1'}$), 148.00 (C_{12}), 147.06 (C_{10}), 146.01 (C_9), 145.58 ($C_{12'}$), 143.35, 143.31 ($C_{h, h'}$), 138.26, 138.23 ($C_{g, g'}$), 138.15 ($C_{3'}$), 133.87 (C_{11}), 133.62 (C_3), 133.05, 133.00 ($C_{a, a'}$), 131.49 ($C_{11'}$), 131.13 ($C_{i, i'}$), 127.52 ($C_{e, e'}$), 126.32 ($C_{2', b, b'}$), 125.93 (C_2), 123.16 ($C_{c, c'}$) 120.21 (C_4), 119.72 (C_6), 119.29 (C_7), 118.95 (C_8), 117.14 (C_{14}), 111.56 ($C_{d, d'}$), 107.94, 107.92 ($C_{f, f'}$). MS (FAB): m/z 810 $[M]^+$.

Preparation of [H_2-3c](PF_6)

The procedure was of the same as for **[H_2-3a]**(PF_6) using dimer **1c** (60 mg, 0.056 mmol), H_2-phencat (60 mg, 0.146 mmol) and KPF_6 (25.7 mg, 0.139 mmol) and after work up gave **[H_2-3c]**(PF_6) as a yellow solid (87 mg, 80%). Anal. Calcd for $C_{41}H_{29}N_5O_3IrPF_6$: C, 50.41, H, 2.99, N, 7.17. Found: C, 50.32, H, 2.93, N, 7.11%. ^{1}H NMR (400 MHz, MeOD): δ 8.90 (1H, dd, J = 8.6, 1.2, H_3), 8.87 (1H, s, H_4), 8.69 (1H, dd, J = 8.6, 0.8, $H_{3'}$), 8.41 (1H, dd, J = 5.1, 1.2, H_1), 8.29 (1H, dd, J = 5.1, 1.6, $H_{1'}$), 8.13 (2H, bd, J = 8.2, $H_{e, e'}$), 7.96 (1H, dd, J = 8.2, 5.1, H_2), 7.88–7.84 (3H, m, $H_{2', d, d'}$), 7.82, 7.80 (2H, 2 × td, J = 7.4, 1.6, $H_{f, f'}$), 7.60 (1H, dd, J = 8.2, 1.6, H_6), 7.49 (2H, bd, J = 5.8, $H_{h, h'}$), 7.11–7.03 (3H, m, $H_{8, c, c'}$), 6.97–6.90 (4H, m, $H_{b, b', g, g'}$), 6.84, (1H, t, J = 7.8, H_7), 6.42, 6.40 (2H, 2 × dd, J = 7.4, 0.8, $H_{a, a'}$). ^{13}C NMR: 167.99, 167.95 ($C_{k, k'}$), 167.73 (C_{13}), 151.04 (C_1), 150.08 ($C_{1'}$), 149.74, 149.40 ($C_{i, i'}$), 148.71 ($C_{h, h'}$), 147.31 (C_{12}), 147.11, (C_{10}), 146.03 (C_9), 144.84 ($C_{12'}$), 144.06, 144.01 ($C_{j, j'}$), 138.23 ($C_{f, f'}$), 138.08 ($C_{3'}$), 133.54 (C_3), 131.59, 131.52 ($C_{a, a'}$), 131.37 ($C_{11'}$), 130.18, 130.14 ($C_{b, b'}$), 127.67 (C_{11}), 126.72 ($C_{2'}$) 126.32 (C_2), 124.63 ($C_{d, d'}$), 123.04, 123.01 ($C_{g, g'}$), 122.43 ($C_{c, c'}$), 120.27 (C_4), 119.74 (C_6), 119.61 ($C_{e, e'}$), 119.24 (C_7), 118.91 (C_8), 116.90 (C_{14}). MS (FAB): m/z 832 $[M]^+$.

General titration procedure

Unless otherwise stated, the following general conditions apply. All titrations were carried out in air at room temperature in 10 mm quartz cuvettes. The solvent system used consisted of a mixture of acetonitrile and water (20 : 1). Adjustments to the pH were carried out with 0.6 M and 0.1 M solutions of HCl in this solvent system and 0.6 M, 0.1 M and 0.05 M solutions of tetramethyl ammonium hydroxide [(Me_4N)OH] in water. pH values were determined using a WTW Profilab pH 597 pH meter with a Mettler Toledo Inlab 422 electrode and are given as measured in the solvent system. The concentrations of **[H_2-3a**, **3c** and **3d]** were made to 0.015 mM, 0.041 mM and 0.083 mM, respectively. These concentrations gave an absorbance within the Beer–Lambert range. The excitation wavelength was set to 326 nm, 330 nm and 400 nm for **[H_2-3a**, **3c** and **3d]**, respectively. Excitation and emission spectra were corrected for the photomultiplier response and are smoothed.

Determination of pH profiles

The solution of the sensors was adjusted to the starting pH value in the acidic range using the standard acid (mentioned above) and a spectrum was recorded. Small aliquots of base were added to the sample. The pH of the solution was allowed to stabilise before each spectrum was recorded. The spectra were recorded at intervals of approximately 0.5 pH units, across the pH range of *ca.* 1–10. Analogous titrations were conducted in the presence of stoichiometric quantities of molybdate. An aqueous standard solution of Na_2MoO_4 was used for this purpose.

Metal-to-Sensor titrations

Titrations for the determination of the composition of the complexes were conducted using the following procedure. The standard sample solutions (0.02 mM, 0.042 mM and 0.083 mM for **[H_2-3a**, **3c** and **3d]**(PF_6), respectively) of the sensors were buffered with 10 μL of 2, 4-lutidine, and the pH was adjusted to the required value (4.08 for **[H_2-3a**, and **3d]**, and 4.67 for **[H_2-3c]**) with standard acid and base solutions. To the above solutions, 5 μL aliquots of the standard solution of Na_2MoO_4 (0.6 mM, 1.26 mM and 2.49 mM for **[H_2-3a**, **3c** and **3d]** respectively) were added. After each addition, the sample was stirred for *ca.* 3 min to allow the solution to equilibrate before the emission was recorded. Aliquots of Na_2MoO_4 were added until an approximate 1 : 1 ratio was reached.

X-ray crystal structure determination of [Me_2-2b](PF_6)

Data were collected on a Bruker Apex 2000 CCD diffractometer using graphite monochromated Mo-Kα radiation, λ = 0.7107 Å. The data were corrected for Lorentz and polarisation effects and empirical absorption corrections were applied. The structure was solved by direct methods and with structure refinement on

F^2 employed SHELXTL version 6.10[29] Hydrogen atoms were included in calculated positions (C–H = 0.93–1.00 Å, O–H = 0.84 Å) riding on the bonded atom with isotropic displacement parameters set to $1.5U_{eq}$ (O) for hydroxyl H atoms, $1.5U_{eq}$ (C) for methyl hydrogen atoms and $1.2U_{eq}$ (C) for all other H atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters without positional restraints. Disordered solvent was removed the Squeeze option in PLATON.[30] Figures were drawn using the program ORTEP.[31] Crystal data for **[Me$_2$-2b]**(PF_6): $C_{43}H_{38}Cl_5F_6IrN_7O_3P$, M = 1215.22, monoclinic, a = 24.571(6) Å, b = 12.865(2) Å, c = 29.199(6) Å, α = 90°, β = 99.084(5)°, γ = 90°, V = 9114(3) Å^3, T = 150(2)K, space group $C2/c$, Z = 8, μ(Mo-Kα) = 0.519 mm^{-1}, 8945 reflections measured, 8945 independent reflections (R_{int} = 0.0000). reflections measured, 8945 independent reflections (R_{int} = 0.0000). The final R_1 values were 0.0433 ($I > 2\sigma(I)$) and 0.0653 (all data). The final $wR(F^2)$ values were 0.0846 ($I > 2\sigma(I)$) and 0.0888 (all data). The goodness of fit on F^2 was 0.856.

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