Observation of an inversion in photophysical tuning in a systematic study of luminescent triazole-based osmium(II) complexes

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Abstract

In a systematic survey of luminescent *bis*(terdentate) osmium(II) complexes a tipping-point involving reversal in photophysical tuning is observed whereby increasing stabilisation of the ligand-based LUMO results in a blue-shift in optical absorption and emission bands. The complexes [Os(N[^]N'[^]N'')₂]²⁺ (N[^]N'[^]N'' = 2,6-bis(1-phenyl-1,2,3-triazol-4-yl)pyridine (**Os1**); 2,6-bis(1-benzyl-1,2,3-triazol-4-yl)pyrazine (**Os2**); 6-(1-benzyl-1,2,3-triazol-4-yl)-2,2'-bipyridyl (**Os3**); 2-(pyrid-2-yl)-6-(1-benzyl-1,2,3-triazol-4-yl)pyrazine (**Os4**); 2-(pyrazin-2-yl)-6-(1-benzyl-1,2,3-triazol-4-yl)pyridine (**Os5**); 6-(1-benzyl-1,2,3-triazol-4-yl)-2,2'-bipyrazinyl (**Os6**)) have been prepared and characterised and all complexes display phosphorescence ranging from the orange to near-IR regions of the spectrum. Replacement of the central pyridine in the ligands of **Os1** by the more π -accepting pyrazine in **Os2** results in a 55 nm red-shift in the ³MLCT-based emission band whilst a larger red-shift of 107 nm is observed for replacement of one of the triazole donors in the ligands of **Os1** by a second pyridine ring in **Os3** ($\lambda_{\text{max}}^{\text{em}} = 702$ nm). Interestingly, replacement of the central pyridine ring in the ligands of **Os3** by pyrazine **Os4** ($\lambda_{\text{max}}^{\text{em}} = 702$ nm) fails to result in a further red-shift in the emission band. Reversal of the relative positions of the pyridine and pyrazine donors in **Os5** ($\lambda_{\text{max}}^{\text{em}} = 733$ nm) compared to **Os4** does indeed result in the expected red-shift in emission with respect to that for **Os3** based on the increased π -acceptor character of the ligands present. However, an inversion in emission tuning

is observed for **Os6** in which the incorporation of a second pyrazine donor in the ligand architecture results in a *blue*-shift in optical absorption and emission maxima ($\lambda_{\text{max}}^{\text{em}} = 710 \text{ nm}$). Electrochemical studies reveal that whilst incorporating pyrazine into the ligands indeed results in an expected anodic shift in the first reduction potential through stabilisation of the ligand-based LUMO, there is also concomitant anodic shift in the Os(II)/Os(III)-based oxidation potential. This stabilisation of the metal-based HOMO thus nullifies the effect of the stabilisation of the LUMO in **Os4** compared to **Os3** resulting in these complexes having coincident emission maxima. For **Os6** the stabilisation of the HOMO through incorporation of two pyrazine donors in the ligand structure now exceeds the stabilisation of the LUMO resulting in a larger HOMO-LUMO gap and the counter-intuitive blue-shift in optical properties in comparison with **Os5**. Whilst it is known that replacement of ligands (e.g. replacing bipyridyl with bipyrazinyl) can result in a larger HOMO-LUMO energy gap through greater stabilisation of the HOMO, these results importantly allow us to capture the tipping-point at which this inversion in photophysical tuning occurs. This therefore enables us to explore the limits available in emission tuning with a relatively simple and minimalist ligand structure.

Introduction

Transition metal complexes exhibiting phosphorescence in the red / near infra-red (NIR) region have been the subject of extensive research.¹ For example, red and NIR emitters have been widely investigated as the phosphor within light emitting electrochemical cells (LECs)²⁻⁷ and organic light emitting devices (OLEDs)⁸⁻¹³, including functioning as the low-energy aspect within multi-component white light systems¹⁴⁻¹⁸, in addition to finding use as luminescent chemosensors.¹⁹⁻²¹ There has also been a notable drive towards the development of complexes which not only display red/NIR emission but also absorb light at longer wavelengths. These photophysical characteristics are ideal for achieving effective luminescent cellular imaging agents, where the occurrence of both the absorption and emission of light within the biologically transparent region is highly desirable.²²⁻²⁵ Further, coordination complexes with electronic absorption profiles extending into the NIR have additionally been identified as necessary in order to improve the efficiency of dye sensitised solar cells (DSSCs), harvesting photons from an often neglected region of the solar emission spectrum.²⁶⁻²⁸

Over the last few decades considerable attention has been paid to coordination complexes of kinetically inert d^6 metals such as Re(I), Ru(II), Ir(III) and Os(II).²⁹ The photophysical properties of these complexes are well understood and documented, with the excited state frequently dominated by long-lived triplet metal-to-ligand charge transfer states ($^3\text{MLCT}$) from which phosphorescence occurs and from where further electron transfer events are possible. With a view towards achieving low energy photoluminescence and potential applications in luminescence cellular imaging, complexes of Os(II) offer several advantageous photophysical properties. Firstly, the high spin-orbit coupling constant associated with the heavy metal centre gives rise to formally spin-forbidden ground state-to- $^3\text{MLCT}$ state electronic absorption bands of appreciable extinction coefficient which occur at significantly lower energy than the corresponding spin-allowed transitions which populate $^1\text{MLCT}$ states.³⁰ Further, these excitation bands are typically red-shifted compared with those observed for comparable complexes of the Group 8 congener Ru(II), with photoluminescence from Os(II) complexes occurring in the deep-red to near-IR spectral region. For example, *bis*-terdentate complexes of Os(II) featuring 6-(5-(trifluoromethyl)pyrazol-3-yl)-2,2'-bipyridine ligands have previously been reported displaying appreciable panchromatic electronic absorption profiles and low-energy luminescence with $\lambda_{\text{em}} = 655\text{-}935\text{ nm}$.³¹ These properties are ideal for potential cellular imaging agents, enabling a greater depth of tissue penetration for excitation, reducing biological damage through use of lower energy excitation sources and avoiding auto-fluorescence from chromophores within the biological material.

Whilst complexes of d^6 metals, particular those of Ru(II) and Ir(III), have been extensively developed for luminescence biological imaging applications, the use of Os(II) complexes for this purpose is rather rare. Keyes and co-workers³² have reported an Os(II) polypyridyl polyarginine conjugate for live cell imaging, whilst Chao and co-workers³³ have investigated a benzimidazolylpyridine-containing Os(II) complex as a lysosomal tracker which displays deep-red emission with $\lambda_{\text{em}} = 736\text{ nm}$. Very recently Zhang and co-workers³⁴ have reported emissive Os(II) polypyridyl complexes featuring iminopyridine ligands which permit NIR luminescence imaging of RNA and nucleoli of live cells. Our own group have previously investigated 1,2,3-triazole-based complexes of Os(II), with complexes in the series $[\text{Os}(\text{bpy})_{3-n}(\text{pytz})_n]^{2+}$ ($\text{bpy} = 2,2'$ -bipyridyl, $\text{pytz} = 1\text{-benzyl-4-(pyrid-2-yl)-1,2,3-triazole}$, $n = 0\text{-}3$) displaying phosphorescence within the deep-red spectral region.³⁵ The homoleptic species $[\text{Os}(\text{pytz})_3]^{2+}$ was found to result in luminescent staining of lysosomes and endosomes within two cancer cell lines. In a related study we have also prepared

the Os(II) complex $[\text{Os}(\text{btzpy})_2]^{2+}$ of the terdentate ligand 2,6-*bis*(1-phenyl-1,2,3-triazol-4-yl)pyridine (btzpy) which displays emission at 595 nm and preferentially localises within the mitochondria of HeLa and U2OS cell lines, allowing for luminescence imaging by confocal microscopy.³⁶ These initial studies also revealed that the homoleptic triazole-containing complexes exhibited significant luminescence quenching in the presence of oxygen with the sensitisation of singlet oxygen thus providing the basis for development of potential dual-mode photodynamic theranostic agents.

Whilst offering promise, the absorption and emission bands exhibited by the complexes in our initial investigations were not ideally situated in the optical spectrum so as to optimally align with the biologically transparent window. To expand upon our previous studies we were motivated to design and develop new terdentate ligand architectures in order to shift the absorption and emission characteristics of the resultant Os(II) complexes firmly into the deep-red / NIR region. Due to the synthetic versatility of the 1,2,3-triazole motif for ligand design, the aforementioned singlet oxygen sensitising activity and also the reported facile conjugation of complexes to biologically relevant targeting moieties³⁷ through 1,2,3-triazole-based linkers we were minded to retain this heterocycle in our ligands appearing in the systematic survey reported here. In order to maintain a relatively simple ligand architecture for reasons of facile synthetic accessibility and concerns over resultant complex solubility, these triazole donors were therefore combined in both symmetric and asymmetric terdentate ligands with more electron-withdrawing pyridine and pyrazine donor rings. Through this approach we were confident of achieving a lowering of the energy of the ligand-based lowest unoccupied molecular orbital (LUMO) and thus red-shift the optical absorption and emission bands of the complexes.

Whilst the parent terdentate ligand 2,2':6',2''-terpyridine (tpy) is ubiquitous in the coordination chemistry of photoactive metal complexes, we note that derivatives and analogues often carry peripheral substituents, primarily upon the pyridyl rings, with the core of the ligand framework remaining intact.³⁸ Less attention has been paid to the synthesis and development of unsubstituted tpy analogues containing higher azines or alternative *N*-donor heterocycles. Pyrazine-based ligands in complexes of Os(II) are relatively rare in the literature but have been reported, for example, in investigating electron transfer and delocalisation³⁹, in addition to featuring within higher chelating ligand structures facilitating coordination to two metal centres

and thus the formation of bi- and multi-metallic systems.⁴⁰ The group of Brewer has extensively explored the use of the 2,3-bis(2-pyridyl-pyrazine) ligand^{41, 42}, including in Os(II)-containing multi-metallic systems displaying NIR absorption⁴³, whilst Campagna and co-workers have utilised the same framework and derivatives thereof in the synthesis of multi-metallic dendrimers which function as light-harvesting antenna.⁴⁴ Whilst the use of pyrazine as a bridging ligand is more widespread, its employment within polyazine ligands of mono-metallic complexes is relatively sparse. For example Ruminski and co-workers have investigated a homoleptic Os(II) complex of dipyrido-2,3-a;3',2'-j-phenazine [Os(dpop')₂]²⁺ which has an UV-Visible absorption profile extending to ~800 nm and displays weak phosphorescence with $\lambda_{em} = 795$ nm.⁴⁵

In this contribution we explore the design and synthesis of new symmetrical and asymmetrical terdentate ligand architectures featuring pyridine, pyrazine and 1,2,3-triazole donor moieties and investigate their coordination chemistry with Os(II). These *bis*-terdentate complexes are emissive in the red/NIR region, with not only the identity but the specific positioning of the azines within the ligand framework having a significant effect upon the photophysical and electrochemical properties of the complexes as a whole. Further, we show that whilst the expected increase in electron withdrawing character does indeed stabilise the LUMO of the complexes, incorporation of pyrazine donors also has a significant stabilising effect on the predominantly osmium d-orbital-based highest occupied molecular orbital (HOMO). Thus we observe a tipping point in our series where the stabilisation of the HOMO outweighs the stabilisation of the LUMO and the trend in photophysical tuning becomes inverted.

Results and Discussion

In similar fashion to the previously reported synthesis of **1**,^{46, 47} the pyrazine-containing ligand **3** was conveniently prepared through the copper-catalysed alkyne-azide cycloaddition (CuAAC) of 2,6-*bis*(ethynyltrimethylsilyl)-pyrazine (**2**) and benzyl azide (Scheme 1). The ¹H NMR spectrum of **3** is simple, with singlets at δ 8.05 and 9.30 corresponding to the triazole-ring and the equivalent pyrazinyl protons respectively. The methylene protons of the benzyl substituents are observed as a further singlet at δ 5.59 whilst the benzylic aromatic protons fall within the multiplets at δ 7.26-7.43.

Scheme 1 The synthetic route to terdentate ligands **1** and **3**

Scheme 2 The synthetic route to terdentate ligands **7** and **10**

The 1,2,3-triazole-appended 2,2'-bipyridyl ligand **7** was prepared *via* a four-step procedure starting from 2-bromopyridine (Scheme 2). Briefly, Pd-catalysed Stille cross-coupling of the stannane **4** with a stoichiometric quantity of 2,6-dibromopyridine afforded 6-bromo-2,2'-bipyridyl (**5**) which subsequently underwent Pd-catalysed Sonogashira cross-coupling with ethynyltrimethylsilane to give the corresponding ethynyl-substituted bipyridine **6**. A further CuAAC reaction with benzyl azide furnished the desired ligand **7** with a modest yield of 44 %. We were additionally able to introduce a pyrazine heterocycle into the terdentate ligand structure (**10**) by following an analogous synthetic route utilising 2,6-dibromopyrazine (Scheme 2). ¹H NMR spectra of the ligands **7** and **10** feature the characteristic singlet triazole-ring resonances at δ 8.17 and 8.18 respectively. The placement of the pyrazine ring in the central position of the *tris*-heterocycle ligand **10** leads to a loss of symmetry for the pyrazine moiety, resulting in the observation of two down-field singlet resonances in the ¹H NMR spectrum at δ 9.43 and 9.54 attributed to the 3- and 5-positions respectively, assigned through nOe correlation data.

In order to determine the effect of the relative positions of the pyridine and pyrazine donors upon the photophysical properties of subsequent complexes we targeted ligand **14** featuring a central pyridine and peripheral pyrazine rings (Scheme 3). An obvious synthetic strategy would be one directly analogous to that described above, employing a stannyl-pyrazine reagent. However, despite reports concerning the preparation of 2-(tributylstannyl)-pyrazine,^{48, 49} we were unable to successfully isolate this species in any appreciable

yield. These difficulties, in addition to the inherent toxicity of tin reagents and problems frequently encountered during the purification of Stille cross-coupling products, led us to seek an alternative synthetic solution. Burke and co-workers have recently reported the robust preparation of a range of 2-heterocyclic *N*-methyliminodiacetic acid (MIDA) boronates, suitable as coupling partners in Pd-catalysed cross-coupling reactions.⁵⁰ Whilst 2-heterocyclic boronic acids are generally unstable and difficult to handle, MIDA boronates are found to be both air and moisture stable and are readily prepared. These reagents have additionally been trialled within Suzuki-type reactions where they have proven effective in providing *in situ* ‘slow release’ of unstable but reactive boronic acids, thereby functioning as effective building blocks in the synthesis of a range of heterocyclic organic frameworks.⁵¹

Scheme 3 Synthesis of the terdentate ligands **14**, **17** and **18**

The 2-pyrazinyl MIDA boronate (**11**) was prepared *via* the reported procedure⁵⁰ and obtained with a yield of 53 %. Initial attempts to cross-couple **11** with a stoichiometric quantity of 2,6-dibromopyrazine gave predominantly the *bis*-substituted product. Consequently, the 1,2,3-triazole moiety was appended first *via* 2-bromo-6-ethynyl-pyridine and subsequent CuAAC reaction with benzyl azide to produce **13** (Scheme 3). Further reaction with pyrazine MIDA-boronate **11** was carried out following a two-pot procedure, successfully furnishing the target ligand **14** with a modest yield of 45 %.

We were additionally able to apply this synthetic methodology and the use of a pyrazinyl MIDA-boronate to produce the triazole-bipyrazine ligand **17** (Scheme 3). The triazole-ring proton of **17** is readily observed in the ¹H NMR spectrum as a singlet at δ 8.91, assigned through a strong nOe correlation with the methylene

protons of the benzyl group, themselves giving rise to a singlet at δ 5.79. COSY spectra allow the protons on the 5- and 6-positions of the peripheral pyrazine ring to be identified as a pair of strongly coupled resonances at δ 9.62 and 8.72, with the proton on the 3-position together with those of the central pyrazine ring appearing as three singlet resonances at δ 9.44, 9.37 and 8.74. The lack of coupling interactions and absence of obvious correlation signals in NOESY NMR spectra precludes the specific assignment of these resonances.

Finally, **11** was utilised further to access the *tris*-pyrazinyl ligand **18** (Scheme 3). Surprisingly, only two reports have previously been made concerning the synthesis of this polyaza species^{38, 49}, both of which rely on the Stille coupling of a stannyl-pyrazine with chloro-pyrazines. Here, the employment of Suzuki coupling of **11** with 2,6-dibromopyrazine gives **18** with a moderate yield of 28 %.

Figure 1 Structures of the Os(II) complexes investigated in this work

The osmium(II) complexes of the reported terdentate ligands (**Os1–Os6**) (Figure 1) were all conveniently prepared as their hexafluorophosphate salts by reaction of two equivalents of the appropriate ligand with $[\text{OsCl}_6][\text{NH}_4]_2$ in refluxing ethylene glycol followed by treatment with NH_4PF_6 . Purification by either column chromatography or recrystallisation gave the *bis*-terdentate complexes as brown to dark-green coloured powders. ^1H NMR analysis of the complexes gave spectra similar to those of the free ligands, although with protons on the coordinating fragments being marginally deshielded. For example, the triazole ring and pyrazinyl protons of ligand **3** are observed at δ 8.37 and 9.18 respectively in $\text{d}_3\text{-MeCN}$, whilst the corresponding resonances for **Os2** appear at δ 8.66 and 9.28. Attempts were also made to prepare the *bis*-

terdentate osmium (II) complex of 2,2':6',2''-terpyrazine (**Os7**) both in an analogous manner to **Os1-Os6** and *via* an alternative route involving reaction between [$\text{Os}(\text{C}_6\text{H}_6)\text{Cl}_2$]₂ and four equivalents of ligand **18** in refluxing EtOH/H₂O. All synthetic attempts resulted in the production of a very dark green intractable powder which remained highly insoluble after metathesis with NH_4PF_6 and $\text{NH}_4\text{BAr}^{\text{F}}_4$ salts. Indeed, very poor solubility has been encountered previously in complexes of this terpyrazine ligand.³⁸ We have thus been unable to confirm the successful synthesis of **Os7** and so discount it from further experimental discussions.

Figure 2 UV-Visible electronic absorption spectra recorded for MeCN solutions of **Os1-Os6** (inset: magnification of the region containing bands for direct singlet ground state to ³MLCT state transitions).

UV-Visible electronic absorption spectra were recorded for acetonitrile solutions of **Os1-Os6** and are shown in Figure 2, with summarised spectroscopic data presented in Table 1. The spectrum of **Os2** exhibits an intense absorbance at 302 nm which is assigned to a $\pi \rightarrow \pi^*$ transition localised on the ligand (**3**), shifted to lower energy compared to a similar ligand-based transition observed for the previously reported complex **Os1** (297 nm).³⁶ **Os2** displays further electronic absorbance features within the visible region, with those between 370-450 nm assigned to ¹MLCT transitions and weaker bands at 520-630 nm attributed to direct population of ³MLCT states, an electronic absorbance feature characteristic of Os(II) polypyridyl-type complexes as a consequence of the high spin-orbit coupling constant of the metal centre.^{30, 52} The ^{1,3}MLCT bands observed for **Os2** are shifted to lower energy compared to those of **Os1**, indicative of a lower energy LUMO as the pyridine moiety is replaced with the more π -accepting pyrazine.

Electronic absorption spectra of **Os3-Os6** are panchromatic, displaying intense absorbance bands in the UV-region in addition to strong bands within the visible which tail-off at ~700 nm. For **Os3**, an intense band centred at 302 nm is assigned to $\pi \rightarrow \pi^*$ intraligand transitions, whilst the $^1\text{MLCT}$ and $^3\text{MLCT}$ absorption envelopes are observed within the regions 400-500 nm and 550-680 nm respectively. These charge transfer bands are stabilised in energy with respect to **Os1-Os2**, primarily a consequence of the partial replacement of 1,2,3-triazole moieties with pyridyl units and subsequent stabilisation of the ligand-based LUMO. Incorporation of more efficient π -accepting units in the form of pyrazine into the ligand set of complex **Os4** may be reasonably expected to further stabilise the $^{1,3}\text{MLCT}$ states. However, when the absorbance profile of **Os4** is compared to that of **Os3**, the positions of the charge transfer bands appear to be unchanged. Moving from **Os4** to **Os5**, where the positions of the pyridyl and pyrazinyl units within the ligands are exchanged, it is likely that the LUMO remains mostly pyrazine-based and as such is now positioned much further away from the 1,2,3-triazole unit which has an appreciable destabilising influence as a consequence of its poor π -acceptor ability. This therefore might be expected to lead to a reduction in the energy of the LUMO for **Os5** over that of **Os4**. Indeed, in agreement with this reasoning the $^{1,3}\text{MLCT}$ bands of **Os5** appear at lower energy with respect to those of **Os4**, with the $^1\text{MLCT}$ maximum recorded at 471 nm and the $^3\text{MLCT}$ absorbance tailing-off beyond 720 nm. Whilst **Os6** with its *bis*-pyrazinyl-containing ligands may be reasonably expected to give further stability to charge transfer transitions, it is interesting to note that the $^{1,3}\text{MLCT}$ bands are of a similar spectral position to those recorded for **Os3** and **Os4**, and are in fact *blue-shifted* relative to those of **Os5**.

Table 1 Summarised photophysical data for **Os1-Os6**

	$\lambda_{\text{abs}}^a / \text{nm}$ ($\epsilon / \text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$)	$\lambda_{\text{em}}^a / \text{nm}$ (R.T.)	$\phi_{\text{em}}^{a,b} / \%$ (Air)	$\phi_{\text{em}}^{b,c} / \%$ (Degassed)	$\tau_{\text{em}}^a / \text{ns}$ (Air)	$\tau_{\text{em}}^c / \text{ns}$ (Degassed)	$\lambda_{\text{em}}^d / \text{nm}$ (77 K)
Os1	530 (2960), 436 (5570), 385 (19400), 338 (13550), 297 (68475), 288 (48600), 242 (49000)	595 ^e	0.8	9.3	63	937	564, 606
Os2	570 (2400), 452 (3900), 409 (14550), 339 (7900), 302 (37300), 248 (25800), 229 (33260)	650 ^f	1.1	3.5	269	924	625, 673(sh)
Os3	631 (2830), 581 (3320), 462 (10450), 400 (9900), 302 (67550), 268 (27775), 259 (34930)	702 ^g	1.0	2.9	88	253	676, 741(sh)
Os4	633 (2480), 587 (2620), 493 (4330), 442 (13280), 312 (52125), 265 (30650), 243 (33970)	702 ^g	1.2	2.5	155	240	687, 746(sh)
Os5	656 (2910), 596 (3320), 523 (4735), 471 (10500), 441 (9430), 405 (8850), 358 (10675), 315 (54075), 263 (40435)	733 ^g	1.1	1.8	135	216	703, 769(sh)
Os6	641 (2230), 590 (2620), 452 (9780), 430 (9750), 396 (8830), 328 (39370), 319 (40025), 269 (33380), 243 (33000)	710 ^g	1.7	2.9	186	288	690, 752(sh)

^a aerated MeCN; ^b relative to $[\text{Ru}(\text{bpy})_3][\text{PF}_6]_2$ $\Phi_{\text{em}} = 0.018$ in aerated MeCN;⁵³ ^c degassed MeCN; ^d 4:1 EtOH/MeOH; ^e $\lambda_{\text{ex}} = 500$ nm; ^f $\lambda_{\text{ex}} = 550$ nm; ^g $\lambda_{\text{ex}} = 580$ nm.

Figure 3 Normalised corrected emission spectra recorded for aerated MeCN solutions of **Os1-Os6** at room temperature.

Complexes **Os1-Os6** were found to be emissive in aerated MeCN solutions from the orange to the deep-red/near infra-red spectral regions (Figure 3 and Table 1), with broad, featureless bands suggesting that the luminescence originates from states having predominantly ³MLCT character. It is pertinent to note that the emissive ³MLCT state in **Os3-Os6** can be accessed through direct excitation into the spin-forbidden ³MLCT

absorption band at wavelengths ≥ 600 nm, ideal for biological imaging applications for example where excitation within the biological transparent region is highly desirable. The emission intensity is affected by the presence of oxygen in all cases, however, the level of quenching in aerated compared to degassed solutions generally diminishes as emission bands become progressively more red-shifted and the lifetime of the excited state becomes shorter. **Os2** exhibits an emission maximum at 650 nm, shifted by some 1420 cm^{-1} (55 nm) to lower energy than **Os1** as a result of replacement of the central pyridyl moiety with pyrazine and the subsequent stabilisation of the $^3\text{MLCT}$ state. This observation is in agreement with UV-Visible electronic absorption data (*vide supra*) and the expectation of a significantly stabilised ligand-based LUMO. Emission bands for **Os3-Os6** are red-shifted still further, with emission maxima beyond 700 nm placing the observed phosphorescence within the near-infrared region. In accordance with their electronic absorption spectra, **Os3** and **Os4** have identically positioned emission maxima ($\lambda_{\text{em}} = 702$ nm), whereas the lower-lying $^3\text{MLCT}$ state in **Os5** results in lower energy emission with a maximum at 733 nm. It is noteworthy that the specific placement of the three heterocycles within the isomeric terdentate ligands of **Os4** and **Os5** has an appreciable influence upon the photophysical properties, with a flanking pyrazine moiety evidently resulting in a more stabilised LUMO. Mirroring the unexpectedly blue-shifted charge-transfer absorption bands recorded for **Os6** relative to those of **Os5**, emission from **Os6** is noted at 710 nm. These observations clearly indicate that the $^3\text{MLCT}$ state of **Os5** is stabilised over that of **Os6**, despite the ligand-localised LUMO of the latter likely to be lower-lying by virtue of the inclusion of four π -accepting pyrazinyl units. We also note that whilst the emission quantum yield for the lowest energy emitter (**Os5**) is small ($\sim 1\%$) it remains comparable to both other complexes within this series and previously reported Os(II) polypyridyl complexes, particularly those which emit in the deep-red / near infra-red region³¹, which are known to be weak emitters at room temperature.^{7, 30, 35}

Photoluminescence lifetimes were recorded for all complexes **Os1-Os6** in both aerated and degassed MeCN solutions (Table 1). The emission lifetime for each complex was found to be elongated in the absence of oxygen, indicating the occurrence of luminescence from an excited state of triplet character and confirming our assignment to phosphorescence from a $^3\text{MLCT}$ state. Indeed, we have previously found that **Os1** is an efficient sensitiser of singlet oxygen ($\Phi^1\text{O}_2 = 57\%$) with the intensity of phosphorescence undergoing a 43-fold reduction between degassed and oxygenated MeCN solutions.³⁶ Further inspection of the degassed

photoluminescence lifetimes for **Os1-Os6** reveal a close agreement with the energy gap law.^{54, 55} Complex **Os1** displays the highest emission energy and correspondingly the longest lifetime of 937 ns, which is seen to shorten across the series as the emission energy decreases. The lowest energy emitter, **Os5**, displays the shortest lifetime of 135 ns, marginally shorter than that of **Os6** where the emission maximum is shifted to slightly shorter wavelength (Figure 3). Photoluminescence quantum yields for degassed solutions are also found to mirror this trend, again in good agreement with the energy gap law, with **Os1** being the most efficient emitter within the series ($\Phi = 9.3\%$), decreasing systematically with the steady reduction in energy of photoluminescence to **Os5** ($\Phi = 1.8\%$).

Low temperature emission spectra were recorded for **Os1-Os6** at 77 K in EtOH / MeOH glass mixtures (Figure S31, Supporting Information). The emission profiles reveal additional vibronic structure, with maxima shifted to higher energy relative to the solution state spectra as a result of rigidochromic effects. Whilst the emission profiles of **Os3** and **Os4** are now separated, with maxima at 676 and 687 nm respectively, the general trend in emission energy across the series remains unchanged in frozen solvent glass, with **Os5** still exhibiting the lowest energy emission with a maximum at 703 nm.

Figure 4 Cyclic voltammograms for 1.5 mmoldm⁻³ MeCN solutions of complexes **Os1-Os6** recorded at r.t. at 100 mVs⁻¹. Solutions contained 0.2 moldm⁻³ NBu₄PF₆ as supporting electrolyte. All potentials are shown against the Fc⁺/Fc couple.

Table 2 Summarised electrochemical data for 1.5 mmoldm⁻³ MeCN solutions of complexes **Os1-Os6** measured at r.t. at a scan rate of 100 mVs⁻¹. Potentials are shown in V vs. Fc⁺/Fc. Anodic-cathodic peak separations ($\Delta E_{a,c}$) for reversible couples are shown in mV within brackets. ($\Delta E_{a,c}$ for Fc⁺/Fc was typically 70 mV).

Complex	E _{ox} / V	E _{red} / V	E _{ox} -E _{red} / V
Os1	+0.64 (67)	-2.00 ^a	2.64
Os2	+0.88 (77)	-1.58 (61), -1.99 ^a	2.46
Os3	+0.56 (72)	-1.67 (67), -1.93 (72)	2.23
Os4	+0.87 (77)	-1.36 (76), -1.72 ^{a,b}	2.23
Os5	+0.80 (76)	-1.31 (66), -1.61 (66)	2.11
Os6	+1.09 (68)	-1.09 (77), -1.39 (69), -2.07 (83)	2.18

^a Cathodic peak potential, ^b Process not shown in Figure 4, see supporting information, Figure S32.

Cyclic voltammograms recorded for complexes **Os1-Os6** are shown in Figure 4 with summarised electrochemical data presented in Table 2. At least one reduction process is observed for each complex **Os1-Os6** within the available electrochemical solvent window, all of which are assigned to ligand-based processes. The trend in potential of the reductive electrochemistry is generally in agreement with our initial expectations. Replacement of the central pyridine in the ligands of **Os1** by pyrazine in the ligands of **Os2** results in an anodic shift of 0.42 V. The first reductions for **Os4** and **Os5** appear at more positive potential than that of **Os3** due to stabilisation of the ligand-based LUMO, again owing to incorporation of pyrazine donors within the ligand structure. In agreement with earlier interpretations based upon spectroscopic data it is noted that the positioning of the pyrazine moiety in a flanking rather than central position within the ligand structure results in enhanced stabilisation of the LUMO, with the first reduction of **Os5** appearing at slightly more positive potential than that of **Os4**. The presence of two π -accepting pyrazine moieties within each ligand of **Os6** results in the appearance of the most anodically shifted first reduction potential at -1.09 V, in line with the assumption that this ligand results in the most stabilised LUMO of all complexes within the series.

All complexes exhibit a reversible oxidation process which is assigned to the Os(II)/Os(III) couple. Based upon our previous work, together with that of others, we initially expected the potential of this oxidation process, though perturbed, to be but relatively insensitive to the changing nature of the ligands across the series owing to the HOMO being predominantly osmium d-orbital in character.^{7, 12, 35, 56, 57} However, the electrochemical data reveal this couple to also be significantly affected by the incorporation of pyrazine units within the ligand set, with the first oxidation potentials for **Os2** and **Os4-5** appearing within the region +0.80-0.88 V vs Fc⁺/Fc, shifted anodically by ca. 0.25 V compared to those of **Os1** and **Os3**. The use of *bis*-

pyrazinyl-containing ligands within complex **Os6** results in an even greater positive shift in first oxidation potential, appearing at +1.09 V.

It is therefore evident that, unlike in our previous studies where the relative energy of the ligand-based LUMO broadly dictates the overall observed changes and trends in photophysical properties of the complexes, for this series the significant variance in the energy of the HOMO makes a key contribution to the spectroscopic properties. The introduction of one pyrazine ring into the terdentate ligand architectures generally leads to a stabilisation and a red-shift in absorption and emission bands, but the extent of this tuning is undermined by concomitant stabilisation of the HOMO with that of the LUMO. For **Os4** the spectroscopic changes by virtue of the stabilisation of the LUMO with respect to that of **Os3** through replacement of a pyridine by pyrazine are cancelled out by a stabilisation of almost equal magnitude of the HOMO. When two pyrazine rings are incorporated into each ligand in **Os6** the additional stabilisation observed for the HOMO outweighs the stabilisation of the LUMO resulting in an increased HOMO-LUMO gap. Thus, the trend in the HOMO-LUMO energy gap revealed through electrochemistry perfectly matches those trends observed in electronic absorption and luminescence spectra (*vide supra*) and explains the reversal in MLCT energy tuning observed on going from **Os5** to **Os6**.

On examining the literature we note that these results on pyrazine ligand-based stabilisation of the HOMO are in agreement with previously reported data on ruthenium(II) and osmium(II) complexes. Whilst the first reduction potential for $[\text{Ru}(\text{bpz})_3]^{2+}$ (bpz = 2,2'-bipyrazine) appears 0.63 V to more positive potential than that for $[\text{Ru}(\text{bpy})_3]^{2+}$, the Ru(II)/Ru(III) oxidation of the former is anodically shifted to a greater degree (0.71 V)⁵⁸ resulting in a blue-shift in both ¹MLCT absorptions and the ³MLCT-based emission band (from 609 nm for $[\text{Ru}(\text{bpy})_3]^{2+}$ to 600 nm for $[\text{Ru}(\text{bpz})_3]^{2+}$ in water)⁵⁹. An analogous blue-shift in emission is observed for $[\text{Os}(\text{bpz})_3]^{2+}$ (700 nm in acetonitrile) compared to $[\text{Os}(\text{bpy})_3]^{2+}$ (724 nm) where the oxidation potential of the former is anodically shifted by 0.70 V with respect to that of the latter, whilst the first reduction potential of $[\text{Os}(\text{bpz})_3]^{2+}$ is positively shifted by 0.59 V.⁶⁰

Figure 5 Molecular orbital energy level diagram for complexes **Os1** to **Os6** and plots of the HOMO and LUMO orbitals in each case.

To complement and corroborate our experimental spectroscopic and electrochemical studies we carried out density functional theory calculations to determine the nature of the frontier orbitals and the influence of the ligands on their relative energies. The calculated relative energies of the HOMO and LUMO for the series of complexes (Figure 5) are in excellent agreement with the experimental electrochemical data (*vide supra*). Replacement of the central pyridine in the ligands in **Os1** by pyrazine as in **Os2** results in a stabilisation of the LUMO by 0.44 eV with a concomitant lesser stabilisation of the HOMO leading to a reduction in the HOMO-LUMO gap by 0.2 eV. The larger π -system associated with the triazolyl bipyridine ligands in **Os3** results in a comparable stabilisation of the LUMO to that for **Os2** with respect to **Os1**. The results confirm the electrochemical data which shows that the red-shift in the optical absorption and emission profiles for **Os3** derives from the HOMO undergoing little or no modulation in energy by virtue of the number of triazole donors in the ligand set in comparison with **Os1**.

The replacement of either the central or outer pyridine ring by pyrazine in the ligands in **Os4** and **Os5** again leads to stabilisation of the HOMO as well as the LUMO. The HOMO and LUMO in **Os4**, incorporating the pyrazine as the central donor in the terdentate ligands, are each stabilised to the same extent in comparison to the frontier orbitals of **Os3** leading to an almost identical HOMO-LUMO energy gap. This is in agreement

with the electrochemical data and the resultant and unexpected lack of a red-shift in the optical absorption spectrum and a coincident emission maximum for this complex compared to those of **Os3**. Placement of the pyrazine as the outer ring of the terdentate ligands in **Os5** leads to a comparable energy of the HOMO with respect to that of **Os4** but the removal of the destabilising influence of a neighbouring triazole moiety results in a stabilisation of the LUMO by a further 0.1 eV. This is again in agreement with the electrochemical data and the experimentally observed red-shift in the absorption and emission profiles of **Os5** compared to those of **Os4**.

Whilst replacement of both pyridine donors in the ligands for **Os3** with pyrazine in the ligands for **Os6** leads to a significant stabilisation of the LUMO this also leads to a greater stabilisation of the HOMO resulting in an enlargement of the HOMO-LUMO gap when compared to **Os5**. The calculated data are therefore in agreement with the experimental electrochemical data, confirming the observed inverted tuning of the ¹MLCT and ³MLCT energies through increasing the number of π -accepting pyrazine moieties in the ligand architecture.

Whilst we were not able to synthetically isolate the terpyrazine (tpz) complex [Os(tpz)₂]²⁺ (**Os7**) we might predict that it would possess absorption and emission spectra further blue-shifted compared to those of **Os6** based on experimental data for bpz complexes compared to their bpy analogues.⁵⁸⁻⁶⁰ We therefore also optimised the ground state of the complex **Os7** in our DFT calculations in order to determine whether the further inclusion of pyrazine donors into the ligand set would lead to further inverted optoelectronic tuning. Due to problems in converging the ground state geometry D_{2d} symmetry was imposed during the optimisation. The calculated molecular orbital energies confirm the prediction of a further stabilisation in the energy of the LUMO (-3.30 eV) by 0.15 eV relative to that of **Os6**. However, a more significant stabilisation by 0.26 eV of the HOMO is observed (-6.68 eV) leading to an enlargement of the HOMO-LUMO gap of **Os7** by 0.12 eV compared to that of **Os6**. Based on the trends and correlations of calculated data and their agreement with the experimental electrochemical and spectroscopic data for these complexes one could confidently predict that the UV-visible absorption and emission profiles of **Os7** would indeed appear further *blue*-shifted compared to those of **Os6**.

The data presented here, complemented with those previously reported for related bidentate systems, show that whilst the incorporation of pyrazine donors does indeed lead to stabilisation of the ligand-based LUMO

and a resultant red-shift in optical absorption and emission bands this is accompanied by a stabilisation of the HOMO. Increasing the electron-withdrawing character of the ligands may continue to result in red-shifted spectral features until a tipping point is reached whereby further stabilisation of the HOMO exceeds that of the LUMO and is manifested by an inversion in the photophysical tuning behaviour. Through sequential modification of the ligand architecture whereby the π -acceptor character is progressively tuned through variation of the number and positions of pyridine and pyrazine rings, rather than wholesale replacement of oligopyridyl with oligopyrazinyl-based ligands, we are able to capture this tipping point and the associated inversion in photophysical properties.

Conclusions

A series of new phosphorescent osmium(II) complexes have been reported which display emission from the red to the near-IR with emission intensity sensitive to the presence of oxygen. In pushing the absorption and emission maxima towards the biologically transparent window the complexes are attractive potential candidate prototypes for further development of targeted dual-mode theranostic agents for confocal imaging microscopy and photodynamic therapy applications. We will be pursuing this work shortly and will report the results in due course.

Importantly, this systematic survey of the photophysical properties across the series of osmium(II) complexes also reveals an initially unexpected and counterintuitive inversion of spectroscopic tuning with increasing ligand π -acceptor character. Whilst the LUMO in these complexes are progressively stabilised by this approach, a stabilisation in the energy of the HOMO is also observed which reaches a tipping point where-upon stabilisation of the latter out-competes the former leading to an inversion and *blue-shifting* in the tuning of optical absorption and emission properties. This work therefore provides important results with regards to the limitations of photophysical tuning in complexes in which a relatively austere and minimalist electron-withdrawing ligand architecture is incorporated.

Experimental Section

OsI³⁶ and benzyl azide⁶¹ were prepared as previously described. **Caution** *care should be taken in the preparation of triazole-containing compounds utilising organic azide starting materials as these precursors are potentially explosive.* Minimal C atom to N atom ratios of 2.5:1 to 3:1 are recommended to mitigate this risk if the organic azide is to be isolated prior to use rather than prepared and used *in situ*. All reagents were purchased from Alfa Aesar, Acros Organics, Sigma Aldrich and Fluorochem and were used as received. All synthetic manipulations were carried out under an atmosphere of dry N₂ employing standard Schlenk line techniques. Deaeration of solvents (Fisher Scientific) was performed through vigorous bubbling with N₂ for a period of at least 15 minutes. Dry THF was obtained by distillation over CaH₂ and stored under an atmosphere of N₂. Dry DMF was purchased from Acros and stored under an atmosphere of dry N₂. NMR spectra were recorded on a Bruker Ascend 400 MHz spectrometer, with all chemical shifts reported in ppm, calibrated relative to the residual solvent signal (CHCl₃: ¹H: δ 7.26, ¹³C δ 77.16; MeCN: ¹H: δ 1.94, ¹³C: δ 1.32, 118.26; Acetone: ¹H: δ 2.17, ¹³C δ 29.84, 206.26). High resolution mass spectrometry was performed on an Agilent 6210 TOF instrument with a dual ESI source. Cyclic voltammograms were measured using a PalmSens EmStat3 potentiostat with PSTrace electrochemical software (version 4.8). Analyte solutions (typical concentration 1.5 mmol dm⁻³) were prepared using N₂ saturated dry MeCN, freshly distilled from CaH₂. All measurements were conducted at room temperature under a stream of dry N₂ at potential scan rates ranging from 50 to 500 mVs⁻¹. NBu₄PF₆ was used as a supporting electrolyte, being recrystallised from ethanol and oven dried prior to use, with a typical solution concentration of 0.2 mol dm⁻³. The working electrode was glassy carbon, with platinum wire utilised as the counter electrode. The reference electrode was Ag/AgCl, being chemically isolated from the analyte solution by an electrolyte containing bridge tube tipped with a porous frit. Ferrocene was employed as an internal reference, with all potentials quoted relative to the Fc⁺/Fc couple. UV-Visible electronic absorption spectra were recorded on an Agilent Cary-60 spectrophotometer, utilising quartz cuvettes of 1 cm pathlength. Emission spectra were recorded on a Fluoromax-4 spectrophotometer utilising quartz cuvettes of 1 cm pathlength and corrected for both detector response and solvent Raman signals. 'Degassed' solutions were prepared *via* three repeat 'freeze-pump-thaw' cycles. Quantum yields (Φ_{em}) are quoted relative to [Ru(bpy)₃][PF₆]₂ in aerated MeCN, with all

complexes being excited at a single wavelength with common optical density. Quantum yields are thus determined from the ratio of integrated area under the peaks. As emission bands for the Os complexes tail into the near infra-red region, outside the effective range of the spectrophotometer, an experimental uncertainty of $\pm 20\%$ is assumed. Luminescence lifetimes were measured with an Edinburgh Instruments Mini- τ , equipped with a picosecond diode laser (404 nm, 56 ps) excitation source.

Synthesis of 2,6-bis(ethynyltrimethylsilyl)-pyrazine (2)

2,6-Dibromopyrazine (1.50 g, 6.30 mmol), Pd(PPh₃)₂Cl₂ (233 mg, 0.33 mmol, 5 mol%) and CuI (127 mg, 0.66 mmol, 10 mol%) were added to a deaerated mixture of dry THF / Et₃N (1:1 v/v) (50 ml). Ethynyltrimethylsilane (3.6 ml, $\rho = 0.709$ g/ml, 25.9 mmol) was added and the reaction solution stirred at 50 °C for 16 h. The reaction solution was cooled to room temperature, filtered through a short silica pad (2 cm) and the filtrate reduced in volume. Purification was achieved *via* column chromatography (SiO₂, CH₂Cl₂). Yield = 1.11 g, 65 %. ¹H NMR (CDCl₃, 400 MHz): 0.27 (s, 18H), 8.54 (s, 2H). ¹³C NMR (CDCl₃, 101 MHz): -0.35, 100.26, 100.45, 139.32, 146.00. HRMS (ES); *m/z* calc. for C₁₄H₂₁N₂Si₂: 273.1243 (MH⁺), found: 273.1244.

Synthesis of 2,6-bis(1-benzyl-1,2,3-triazol-4-yl)-pyrazine (3)

2,6-Bis(ethynyltrimethylsilyl)-pyrazine (1.10 g, 4.03 mmol), CuSO₄·5H₂O (0.77 g, 3.07 mmol), sodium ascorbate (1.22 g, 6.16 mmol), K₂CO₃ (3.56 g, 25.7 mmol) and benzyl azide (1.37 g, 10.3 mmol) were combined in 1:1 (v/v) THF / H₂O (100 ml). ^tBuOH (20 ml) and pyridine (3.5 ml) were added and the resultant mixture stirred at r.t. for 16 h. The organic solvents were removed by rotary evaporation to leave an aqueous suspension to which was added CHCl₃ (150 ml), additional H₂O (60 ml) and concentrated aq. NH₃ (15 ml). The bi-phasic mixture was stirred rapidly at r.t. for 1 h. The organic layer was separated and washed successively with dilute aq. NH₃ (200 ml), saturated brine (200 ml) and H₂O (200 ml) then dried over MgSO₄ and evaporated to dryness. Purification was performed *via* column chromatography (SiO₂, 1 % MeOH / CH₂Cl₂), affording the title compound as a white solid. Yield = 1.25 g, 79 %. ¹H NMR (CDCl₃, 400 MHz): 5.59 (s, 4H), 7.26-7.34 (m, 4H), 7.34-7.43 (m, 6H), 8.05 (s, 2H), 9.30 (s, 2H). ¹³C NMR (CDCl₃, 101 MHz): 54.56, 122.97, 128.25, 129.08, 129.36, 134.37, 140.87, 144.91, 146.36. HRMS (ES); *m/z* calc. for

C₂₂H₁₉N₈: 395.1727 (MH⁺), found: 395.1729; *m/z* calc. for C₂₂H₁₈N₈Na: 417.1547 (M+Na⁺), found: 417.1547. Anal. Calc'd for C₂₂H₁₈N₈ (%): C 66.99, H 4.60, N 28.41, found (%): C 66.98, H 4.42, N 28.29.

Synthesis of 2-(tri-*n*-butylstannyl)-pyridine (4)

The synthesis was carried out following a previously published procedure⁶²: To a solution of 2-bromopyridine (3 ml, ρ = 1.657 g/ml, 31.5 mmol) in dry THF (120 ml) at -78 °C was added, dropwise, ⁿBuLi (13.3 ml, 2.5 M in hexanes, 33.3 mmol). The mixture was stirred for a further 1 h at -78 °C before the quick addition of tri-*n*-butyl tin chloride (8.6 ml, ρ = 1.2 g/ml, 31.7 mmol). Stirring was maintained at -78 °C for 3 h before the solution was allowed to warm to room temperature and then quenched through the addition of a saturated aqueous solution of NH₄Cl (30 ml). The reaction mixture was extracted into ethyl acetate (3 x 50 ml) with the combined organic layers then washed with saturated brine (100 ml), H₂O (100 ml) and dried over MgSO₄. Evaporation of the solvent *in vacuo* yielded a light brown coloured oil which was stored in the refrigerator and used without further purification. Yield = 11.30 g, 97 %. Characterisation data matched that previously reported.⁶² ¹H NMR (CDCl₃, 400 MHz): 0.84-0.90 (m, 9H), 1.08-1.14 (m, 6H), 1.28-1.37 (m, 6H), 1.50-1.59 (m, 6H), 7.10 (ddd, *J* = 1.3, 4.9, 7.7 Hz, 1H), 7.39 (dt, *J* = 1.2, 7.4 Hz, 1H), 7.48 (td, *J* = 1.7, 7.5 Hz, 1H), 8.73 (d, *J* = 4.8 Hz, 1H).

Synthesis of 6-bromo-2,2'-bipyridine (5)

2,6-Dibromopyridine (5.69 g, 24.0 mmol), 2-(tri-*n*-butylstannyl)-pyridine (8.00 g, 21.7 mmol) and Pd(PPh₃)₄ (1.50 g, 1.30 mmol, 6 mol%) were combined in thoroughly deaerated toluene (30 ml) and heated to reflux for 12 h. After cooling to room temperature, the solvent was removed by rotary evaporation and the resulting residue redissolved in CH₂Cl₂ (30 ml). Extraction of the organic phase with 3 x 50 ml portions of 6M aq. HCl provided an aqueous solution which was subsequently neutralised with 10 % aq. NH₃ solution. The aqueous phase was then extracted with CH₂Cl₂ (3 x 30 ml), with the combined organic layers being washed with H₂O (100 ml), dried over MgSO₄ and evaporated to dryness. Purification was achieved *via* column chromatography (SiO₂, gradient elution, 0.5 % MeOH / CH₂Cl₂ to 1% MeOH / CH₂Cl₂), affording the product as a white solid. Yield = 1.38 g, 27 %. ¹H NMR (CDCl₃, 400 MHz): 7.30-7.35 (m, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.66 (t, *J* = 8.00 Hz, 1H), 7.82 (td, *J* = 1.6, 7.9 Hz, 1H), 8.35-8.43 (m, 2H), 8.66 (d, *J* = 4.5 Hz,

1H). ¹³C NMR (CDCl₃, 101 MHz): 119.86, 121.64, 124.41, 128.13, 137.17, 139.37, 141.74, 149.37, 154.64, 157.50. HRMS (ES); *m/z* calc. for C₁₀H₈N₂Br: 234.9865 (MH⁺), found: 234.9867.

Synthesis of 6-(ethynyltrimethylsilyl)-2,2'-bipyridine (6)

6-Bromo-2,2'-bipyridine (1.22 g, 5.19 mmol), Pd(PPh₃)₂Cl₂ (182 mg, 0.26 mmol, 5 mol%) and CuI (99 mg, 0.52 mmol, 10 mol%) were added to a deaerated 1:1 (v/v) mixture of dry THF / Et₃N (60 ml). Ethynyltrimethylsilane (1.8 ml, ρ = 0.709 g/ml, 13.0 mmol) was added and the reaction solution then heated to 60 °C for 16 h. The reaction mixture was allowed to cool to room temperature, passed through a short (2 cm) silica pad and the filtrate evaporated. The residue was purified *via* column chromatography (SiO₂, 1 % MeOH / CH₂Cl₂) affording the title compound. Yield = 1.09 g, 83%. ¹H NMR (CDCl₃, 400 MHz): 0.29 (s, 9H), 7.27-7.34 (m, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.73-7.83 (m, 2H), 8.35 (d, *J* = 8.0 Hz, 1H), 8.47 (d, *J* = 8.0 Hz, 1H), 8.65 (d, *J* = 4.4 Hz, 1H). ¹³C NMR (CDCl₃, 101 MHz): -0.08, 94.61, 104.12, 120.67, 121.74, 124.10, 127.68, 137.01, 137.08, 142.58, 149.18, 155.54, 156.58. HRMS (ES): *m/z* calc. for C₁₅H₁₇N₂Si (MH⁺): 253.1161, found: 253.1156.

Synthesis of 6-(1-benzyl-1,2,3-triazol-4-yl)-2,2'-bipyridine (7)

6-(Ethynyltrimethylsilyl)-2,2'-bipyridine (1.10 g, 4.36 mmol), benzyl azide (0.57 g, 4.29 mmol), K₂CO₃ (1.19 g, 8.62 mmol), CuSO₄·5H₂O (0.42 g, 1.69 mmol) and sodium ascorbate (0.68 g, 3.43 mmol) were added to 1:1 (v/v) THF / H₂O (100 ml). ^tBuOH (20 ml) and pyridine (3.5 ml) were added and the reaction mixture then stirred for 16 h at r.t. The organic solvents were removed by rotary evaporation to afford an aqueous suspension to which was added CHCl₃ (100 ml), additional H₂O (50 ml) and conc. aq. NH₃ (15 ml). The biphasic mixture was stirred rapidly at r.t. for 40 mins. and the organic layer then separated. The organic phase was washed successively with dilute aq. NH₃ (200 ml), brine (200 ml) followed by H₂O (200 ml) and then dried over MgSO₄. Purification was carried out *via* column chromatography (Al₂O₃, gradient elution, CH₂Cl₂ to 2% MeOH / CH₂Cl₂) giving the product as a white solid. Yield = 0.59 g, 44 %. ¹H NMR (CDCl₃, 400 MHz): 5.62 (s, 2H), 7.27-7.43 (m, 6H), 7.79 (td, *J* = 1.2, 7.8 Hz, 1H), 7.90 (t, *J* = 7.9 Hz, 1H), 8.17 (s, 1H), 8.20 (dd, *J* = 0.8, 7.9 Hz, 1H), 8.32 (dd, *J* = 0.8, 7.7 Hz, 1H), 8.40 (d, *J* = 7.9 Hz, 1H), 8.67 (d, *J* = 4.3 Hz, 1H). ¹³C NMR (CDCl₃, 101 MHz): 54.49, 120.29, 120.32, 121.19, 122.19, 123.90, 128.23, 128.94, 129.31, 134.74, 136.90, 137.96, 149.23, 149.33, 149.76, 155.82, 156.07. HRMS (ES); *m/z* calc. for

C₁₉H₁₆N₅: 314.1400 (MH⁺), found: 314.1402; *m/z* calc. for C₁₉H₁₅N₅Na: 336.1220 (M+Na⁺), found: 336.1220. Anal. Calc'd for C₁₉H₁₅N₅ (%): C 72.83, H 4.83, N 22.35, found (%): C 72.94, H 4.86, N 22.43.

Synthesis of 2-Bromo-6-(pyridin-2-yl)-pyrazine (8)

2,6-Dibromopyrazine (3.55 g, 14.9 mmol), 2-(tributylstannyl)-pyridine (5.51 g, 14.9 mmol) and Pd(PPh₃)₄ (1.07 g, 0.926 mmol, 6 mol%) were added to deaerated toluene (100 ml) and heated at 110 °C for 21 h. The dark red-brown coloured mixture was cooled to room temperature and the solvent removed under reduced pressure. The resulting oily residue was re-dissolved in CH₂Cl₂ (100 ml) and extracted with 2 x 100 ml portions of aq. 6 M HCl. The combined aqueous layers were then neutralised with 30 % aq. NH₃ solution resulting in the formation of a light brown precipitate. The aqueous suspension was extracted with 2 x 100 ml portions of CH₂Cl₂, with the combined organic phases being then dried over MgSO₄ and the solvent removed. Purification was achieved via column chromatography (SiO₂, gradient elution 0.5 % MeOH / CH₂Cl₂ to 0.75 % MeOH / CH₂Cl₂) with the product eluting immediately before a yellow coloured band. The title compound was obtained as a white solid. Yield = 1.50 g, 43 %. ¹H NMR (CDCl₃, 400 MHz): 7.38 (ddd, *J* = 1.2, 4.7, 7.5 Hz, 1H), 7.85 (td, *J* = 1.8, 7.7 Hz, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 8.68-8.72 (m, 2H), 9.56 (s, 1H). ¹³C NMR (CDCl₃, 101 MHz): 122.08, 125.09, 137.32, 140.08, 141.03, 147.03, 149.72, 151.90, 152.87. HRMS (ES); *m/z* calc. for C₉H₇N₃Br: 235.9818 (MH⁺), found: 235.9823.

2-(Ethynyltrimethylsilyl)-6-(pyridin-2-yl)-pyrazine (9)

2-Bromo-6-(pyridin-2-yl)-pyrazine (1.36 g, 5.76 mmol), Pd(PPh₃)₂Cl₂ (215 mg, 0.307 mmol, 5 mol%) and CuI (102 mg, 0.536 mmol, 9 mol%) were added to deaerated 1:1 (v/v) dry THF / Et₃N (80 ml). Ethynyltrimethylsilane (1.6 ml, ρ = 0.709 g/ml, 11.5 mmol) was added and the reaction mixture then stirred at 60 °C for 16 h. The resultant dark brown coloured solution was filtered through a short silica pad and the filtrate evaporated to dryness. Purification was carried out *via* column chromatography (SiO₂, 1% MeOH / CH₂Cl₂), affording the product as a pale yellow oil. Yield = 1.14 g, 78 %. ¹H NMR (CDCl₃, 400 MHz): 0.31 (s, 9H), 7.37 (ddd, *J* = 0.8, 4.8, 7.5 Hz, 1H), 7.84 (td, *J* = 1.7, 7.7 Hz, 1H), 8.42 (d, *J* = 7.9 Hz, 1H), 8.68-8.73 (m, 2H), 9.53 (s, 1H). ¹³C NMR (CDCl₃, 101 MHz): -0.21, 99.50, 101.14, 122.05, 124.81, 137.20, 138.51, 141.71, 147.54, 149.56, 150.64, 153.72. HRMS (ES); *m/z* calc. for C₁₄H₁₆N₃Si: 254.1108 (MH⁺), found: 254.1117.

2-(1-Benzyl-1,2,3-triazol-4-yl)-6-(pyridin-2-yl)-pyrazine (10)

2-(Ethynyltrimethylsilyl)-6-(pyridin-2-yl)-pyrazine (1.14 g, 4.50 mmol) and benzyl azide (610 mg, 4.58 mmol) were added to 1:1 (v/v) THF / H₂O (120 ml). ^tBuOH (20 ml) was added followed by K₂CO₃ (1.08 g, 7.82 mmol), CuSO₄·5H₂O (463 mg, 1.85 mmol), sodium ascorbate (768 mg, 3.87 mmol) and pyridine (3.5 ml). The reaction mixture was stirred rapidly at room temperature for 27 h and the organic solvents then removed *via* rotary evaporation. To the resulting aqueous suspension was then added CHCl₃ (150 ml), additional H₂O (50 ml) and concentrated aq. NH₃ (12 ml). The biphasic mixture was stirred rapidly at room temperature for 1 h and the organic layer separated. The aqueous phase was extracted with a further 2 x 50 ml portions of CHCl₃, with the combined organic layers being then washed successively with dilute aq. NH₃ (2 x 100 ml), brine (1 x 100 ml) and H₂O (100 ml). The organic phase was dried over MgSO₄ and the solvent removed to leave a light brown coloured solid which was purified by column chromatography (SiO₂, gradient elution 1 % MeOH / CH₂Cl₂ to 2.5 % MeOH / CH₂Cl₂) affording the product as an off-white solid after thorough drying *in vacuo*. Yield = 1.09 g, 77 %. ¹H NMR (CDCl₃, 400 MHz): 5.64 (s, 2H), 7.33-7.45 (m, 6H), 7.82 (td, *J* = 1.7, 7.7 Hz, 1H), 8.18 (s, 1H), 8.35 (d, *J* = 7.9 Hz, 1H), 8.71 (d, *J* = 4.6 Hz, 1H), 9.43 (s, 1H), 9.54 (s, 1H). ¹³C NMR (CDCl₃, 101 MHz): 54.46, 121.43, 123.02, 124.49, 128.15, 128.96, 129.25, 134.34, 136.96, 141.44, 141.89, 144.43, 146.56, 149.48, 149.96, 153.97. HRMS (ES); *m/z* calc. for C₁₈H₁₅N₆: 315.1353 (MH⁺), found: 315.1381; *m/z* calc. for C₁₈H₁₄N₆Na: 337.1172 (M+Na)⁺, found: 337.1174.

Synthesis of 2-pyrazinyl MIDA boronate (11)

Following the procedure previously reported by Burke and co-workers⁵⁰: 2-Iodopyrazine (2.0 ml, ρ = 2.086 g/ml, 20.2 mmol) and tris(isopropyl) borate (4.7 ml, ρ = 0.815 g/ml, 20.3 mmol) were added to dry THF (70 ml) and cooled to -78 °C. ⁿBuLi (8.1 ml, 2.5 M in hexanes, 20.2 mmol) was added dropwise and the solution stirred for 1 h at -78 °C and then allowed to warm to r.t. with further stirring for 3 h. Separately, a three-neck flask equipped with a dropping funnel, thermometer and distillation apparatus was charged, under N₂, with a previously prepared solution of *N*-methyliminodiacetic acid (5.35 g, 36.3 mmol) in DMSO (30 ml) which was subsequently heated to 120 °C. The boronate solution was then transferred *via* cannula to the dropping funnel and added to the hot reaction mixture slowly, dropwise, at such a rate so as to maintain the internal

temperature between 110-120 °C. The THF was rapidly distilled during the course of the addition, after which the DMSO solvent was also removed by distillation under reduced pressure at 50 °C. The resulting brown coloured residue was dried under high vacuum overnight at 50 °C. Purification was carried out by column chromatography (SiO₂, gradient elution, 5% MeCN / Et₂O to MeCN), affording the product as a light brown crystalline solid which was stored in the refrigerator. Yield = 2.50 g, 53 %. Characterisation data matched that previously reported.⁵⁰ ¹H NMR (d₃-MeCN, 400 MHz): 2.61 (s, 3H), 4.00 (d, *J* = 16.6 Hz, 2H), 4.18 (d, *J* = 16.9 Hz, 2H), 8.53 (d, *J* = 2.6 Hz, 1H), 8.68 (dd, *J* = 1.6, 2.6 Hz, 1H), 8.77 (d, *J* = 1.6 Hz, 1H).

Synthesis of 2-bromo-6-(1-benzyl-1,2,3-triazol-4-yl)-pyridine (13)

2,6-Dibromopyridine (5.00 g, 21.1 mmol), Pd(PPh₃)₂Cl₂ (730 mg, 1.04 mmol, 5 mol%) and CuI (403 mg, 2.11 mmol, 10 mol%) were added to a deaerated 7:1 (v/v) mixture of dry THF / Et₃N (80 ml). Ethynyltrimethylsilane (2.65 ml, ρ = 0.709 g/ml, 19.1 mmol) was added and the reaction solution stirred at 40 °C for 6 h. The dark brown coloured solution was cooled to r.t., passed through a short (2 cm) silica plug and the filtrate evaporated to dryness. Column chromatography (SiO₂, 3:7 CH₂Cl₂ / hexane) afforded a white solid (1.95 g) which was found by ¹H NMR (CDCl₃) analysis to contain a mixture of the desired 2-bromo-6-(ethynyltrimethylsilyl)-pyridine (**12**) and a small quantity of unreacted 2,6-dibromopyridine, which was used in the subsequent step without further purification, as has been previously reported.⁶³ 2-Bromo-6-(ethynyltrimethylsilyl)-pyridine (**12**) (1.27 g, mixture as detailed above), benzyl azide (0.69 g, 5.18 mmol) and K₂CO₃ (1.55 g, 11.2 mmol) were added to 1:1 (v/v) THF / H₂O (120 ml). ^tBuOH (20 ml) was added followed by CuSO₄·5H₂O (0.65 g, 2.60 mmol), sodium ascorbate (1.00 g, 5.04 mmol) and pyridine (3 ml). The reaction mixture was stirred at r.t. for 23 h after which the organic solvents were removed by rotary evaporation. To the resulting aqueous suspension was then added CHCl₃ (150 ml), additional H₂O (50 ml) and conc. aq. NH₃ (12 ml). The biphasic mixture was stirred rapidly for 1 h at r.t. The organic layer was removed and the aqueous phase extracted with a 50 ml portion of CHCl₃. The combined organic layers were washed with dilute aq. NH₃ (100 ml) followed by brine (100 ml), dried over MgSO₄ and then evaporated to dryness. The crude solids were purified by column chromatography (SiO₂, 1 % MeOH / CH₂Cl₂) to give the title compound as a white powder. Yield = 0.73 g, 46 %. ¹H NMR (CDCl₃, 400 MHz): 5.56 (s, 2H), 7.28-7.35 (m, 2H), 7.35-7.42 (m, 4H), 7.60 (t, *J* = 7.7 Hz, 1H), 8.08 (s, 1H), 8.12 (dd, *J* = 0.6, 7.7 Hz, 1H). ¹³C

NMR (CDCl₃, 101 MHz): 54.57, 118.94, 122.79, 127.09, 128.40, 129.07, 129.34, 134.32, 139.30, 141.75, 147.55, 151.44. HRMS (ES); *m/z* calc. for C₁₄H₁₂N₄Br: 315.0240 (MH⁺), found: 315.0233; *m/z* calc. for C₁₄H₁₁N₄BrNa: 337.0059 (M+Na⁺), found: 337.0053.

Synthesis of 2-pyrazinyl-6-(1-benzyl-1,2,3-triazol-4-yl)-pyridine (14)

Anhydrous Cu(OAc)₂ (146 mg, 0.80 mmol), tribasic K₃PO₄ (780 mg, 3.68 mmol) and ten 4 Å molecular sieves were added to thoroughly deaerated dry DMF (20 ml). Diethanolamine (160 µl, ρ = 1.097 g/ml, 1.67 mmol) was added and the mixture heated to 85 °C for 15 minutes. The resulting deep blue coloured mixture was then transferred *via* cannula to a reaction flask containing 2-bromo-6-(1-benzyl-1,2,3-triazol-4-yl)-pyridine (**13**) (435 mg, 1.38 mmol), 2-pyrazinyl MIDA boronate (**11**) (575 mg, 2.44 mmol), tribasic K₃PO₄ (790 mg, 3.72 mmol), anhydrous KOAc (146 mg, 1.49 mmol), Pd XPhos G1 (77 mg, 0.10 mmol) and ten 4 Å molecular sieves. The reaction mixture was heated to 100 °C for 20 h, cooled to r.t. and then diluted through the addition of CHCl₃ (100 ml) and H₂O (150 ml). The organic layer was separated and the aqueous phase extracted with a further 100 ml portion of CHCl₃. The combined organic layers were then washed with H₂O (2 x 200 ml), dilute aq. NH₃ (2 x 100 ml) followed by brine (100 ml), dried over MgSO₄ and then evaporated to dryness. Purification was carried out by column chromatography (Al₂O₃, gradient elution, 0.1% MeOH / CH₂Cl₂ to 0.2 % MeOH / CH₂Cl₂) giving the product as a white solid. Yield = 194 mg, 45 %. ¹H NMR (CDCl₃, 400 MHz): 5.62 (s, 2H), 7.32-7.44 (m, 5H), 7.91 (t, *J* = 7.9 Hz, 1H), 8.16 (s, 1H), 8.24 (dd, *J* = 0.8, 8.0 Hz, 1H), 8.26 (dd, *J* = 0.8, 8.0 Hz, 1H), 8.57 (d, *J* = 2.5 Hz, 1H), 8.58-8.60 (m, 1H), 9.62 (d, *J* = 1.3 Hz, 1H). ¹³C NMR (CDCl₃, 101 MHz): 54.53, 120.55, 120.90, 122.35, 128.29, 129.01, 129.34, 134.57, 138.13, 143.42, 143.70, 144.58, 148.81, 150.08, 150.99, 153.82. HRMS (ES); *m/z* calc. for C₁₈H₁₅N₆: 315.1353 (MH⁺), found: 315.1350; *m/z* calc. for C₁₈H₁₄N₆Na: 337.1172 (M+Na⁺), found: 337.1164. Anal. Calc'd for C₁₈H₁₄N₆ (%): C 68.78, H 4.49, N 26.73, found (%): C 68.89, H 4.57, N 26.61.

2-Bromo-6-(1-benzyl-1,2,3-triazol-4-yl)-pyrazine (16)

2,6-Dibromopyrazine (7.00 g, 29.4 mmol), Pd(PPh₃)₂Cl₂ (0.94 g, 1.34 mmol, 4.5 mol%) and CuI (0.51 g, 2.68 mmol, 9.1 mol%) were added to a mixture of dry THF (75 ml) and Et₃N (15 ml). Ethynyltrimethylsilane (4.1 ml, ρ = 0.709 g/ml, 29.6 mmol) was added and the reaction solution heated to 30 °C for 6 h. The dark

red-brown coloured solution was cooled to r.t. and filtered through a short silica pad. The filtrate was evaporated to dryness and the resultant residue subject to column chromatography (SiO₂, 7:3 hexane / CH₂Cl₂), affording an orange coloured oil. ¹H NMR analysis revealed the product to be comprised of a mixture of 2,6-dibromo-pyrazine, 2,6-bis(ethynyltrimethylsilyl)-pyrazine, and 2-bromo-6-(ethynyltrimethylsilyl)-pyrazine (**15**) in a 0.5:0.5:1 respective molar ratio. This mixture was used in the following step without further purification. Yield (based on **15**) = 2.90 g, 39%. Relevant ¹H NMR (CDCl₃, 400 MHz) analysis for **15**: 0.28 (s, 9H), 8.58 (s, 1H), 8.59 (s, 1H).

The above mixture of substituted pyrazines (5.50 g, calc'd to contain 2.75 g, 10.8 mmol of 2-bromo-6-(ethynyltrimethylsilyl)-pyrazine (**15**)) was combined with excess benzyl azide (3.31 g, 24.9 mmol), CuSO₄·5H₂O (2.75 g, 11.0 mmol), sodium ascorbate (4.12 g, 20.7 mmol) and K₂CO₃ (5.00 g, 36.23 mmol) in a 1:1 (v/v) solution of THF / H₂O (300 ml). ^tBuOH (30 ml) was added followed by pyridine (6 ml) and the resultant suspension stirred rapidly at room temperature for 18 h. The organic solvent were removed by rotary evaporation to give an aqueous suspension to which was added CHCl₃ (200 ml), conc. aq. NH₃ (20 ml) and additional H₂O (50 ml). The bi-phasic mixture was stirred rapidly at room temperature for 1 h and the organic layer then removed. The aqueous phase was extracted with a further 100 ml portion of CHCl₃ and the combined organic layers then washed successively with dilute aq. NH₃ (10%) (2 x 100 ml) and brine (1 x 100 ml). The organic phase was dried over MgSO₄ and the solvent removed to leave an oily residue which was purified by column chromatography (SiO₂, 1.5 % MeOH / CH₂Cl₂) yielding the title compound as a white solid. Yield = 2.39 g, 70 %. ¹H NMR (CDCl₃, 400 MHz): 5.59 (s, 2H), 7.29-7.35 (m, 2H), 7.36-7.43 (m, 3H), 8.10 (s, 1H), 8.57 (s, 1H), 9.33 (s, 1H). ¹³C NMR (CDCl₃, 101 MHz): 54.66, 123.71, 128.40, 129.20, 129.40, 134.02, 139.75, 140.17, 145.12, 145.98, 146.41. HRMS (ES); *m/z* calc. for C₁₃H₁₁N₅Br: 316.0192 (MH⁺), found: 316.0190; *m/z* calc. for C₁₃H₁₀N₅BrNa: 338.0012 (M+Na⁺), found: 338.0011; *m/z* calc. for C₂₆H₂₀N₁₀Br₂Na: 653.0132 (2M+Na⁺), found: 653.0087.

Synthesis of 6-(1-benzyl-1,2,3-triazol-4-yl)-2,2'-bipyrazine (**17**)

Anhydrous Cu(OAc)₂ (200 mg, 1.10 mmol) and tribasic K₃PO₄ (970 mg, 4.57 mmol) were added to dry, thoroughly deaerated DMF (20 ml) along with ten 4Å molecular sieves. Diethanolamine (210 µl, ρ = 1.097 g/ml, 2.19 mmol) was added and the solution heated to 85 °C with stirring for 10 minutes. The resulting

bright blue coloured solution was then transferred *via* cannula to a reaction vessel containing 2-Bromo-6-(1-benzyl-1,2,3-triazol-4-yl)-pyrazine (**16**) (608 mg, 1.92 mmol), 2-pyrazinyl MIDA boronate (**11**) (661 mg, 2.81 mmol), tribasic K₃PO₄ (800 mg, 3.77 mmol), anhydrous KOAc (184 mg, 1.87 mmol), Pd XPhos G1 (97 mg, 0.13 mmol) and ten 4Å molecular sieves. The reaction mixture was heated to 100 °C for 22 h, cooled to r.t. and then diluted through the addition of CHCl₃ (100 ml) and H₂O (150 ml). The organic layer was removed and the aqueous phase extracted with a further portion (100 ml) of CHCl₃. The combined organic layers were washed successively with H₂O (200 ml), dilute aq. NH₃ (2 x 100 ml) followed by brine (100 ml), dried over MgSO₄ and the solvent removed *in vacuo*. The residue was purified by column chromatography (Al₂O₃, 0.1 % MeOH / CH₂Cl₂) giving an off-white powder. The solids were re-dissolved in CH₂Cl₂ (15 ml) and slowly triturated with excess hexanes to afford the pure title compound as a white solid. Yield = 128 mg, 21 %. ¹H NMR (d₆-Acetone, 400 MHz): 5.79 (s, 2H), 7.33-7.45 (m, 3H), 7.45-7.50 (m, 2H), 8.72-8.75 (m, 2H), 8.91 (s, 1H), 9.37 (s, 1H), 9.44 (s, 1H), 9.62 (d, *J* = 0.9 Hz, 1H). ¹³C NMR (d₆-Acetone, 101 MHz): 54.71, 125.36, 129.09, 129.37, 129.88, 136.82, 142.27, 142.65, 144.20, 145.03, 146.11, 146.59, 146.71, 149.28, 149.99. HRMS (ES); *m/z* calc. for C₁₇H₁₄N₇: 316.1305 (MH⁺), found: 316.1296; *m/z* calc. for C₁₇H₁₃N₇Na: 338.1125 (M+Na⁺), found: 338.1116. Anal. Calc'd for C₁₇H₁₃N₇ (%): C 64.75, H 4.16, N 31.09, found (%): C 64.81, H 3.96, N 31.03.

Synthesis of 2,2':6',2''-terpyrazine (**18**)

2,6-Dibromopyrazine (325 mg, 1.36 mmol), 2-pyrazinyl MIDA boronate (**11**) (1.11 g, 4.72 mmol), tribasic K₃PO₄ (2.14 g, 10.1 mmol), Pd XPhos G1 (80 mg, 0.11 mmol), anhydrous Cu(OAc)₂ (274 mg, 1.51 mmol), diethanolamine (0.3 ml, ρ = 1.097 g/ml, 3.13 mmol) and 20 4Å molecular sieves were added to an oven dried flask. Dry, deaerated DMF (15 ml) was added and the mixture heated to 100 °C for 17 hours. After cooling to r.t. the mixture was diluted through the addition of CHCl₃ (70 ml) and H₂O (100 ml). The organic phase was removed and the aqueous layer extracted with a further 50 ml portion of CHCl₃. The combined organic layers were subsequently washed with dilute aq. NH₃ (100 ml) followed by brine (2 x 200 ml) and dried over MgSO₄. The solvent was removed under reduced pressure and the remaining brown solids dried thoroughly under high vacuum. The crude solids were then suspended in stirring MeOH (30 ml), collected by filtration and washed with hexane to give the pure title compound as beige coloured solids. Yield = 89

mg, 28 %. NMR characterisation was found to be in agreement with that reported in the literature³⁸: ¹H NMR (CDCl₃, 400 MHz): 8.71 (s, 4H), 9.68 (s, 2H), 9.75 (s, 2H). HRMS (ES): *m/z* calc. for C₁₂H₉N₆: 237.0888 (MH⁺), found: 237.0887.

Synthesis of Os2

[(NH₄)₂OsCl₆] (150 mg, 0.34 mmol) and **3** (282 mg, 0.72 mmol) were combined in ethylene glycol (25 ml) and heated to reflux for 16 h. The reaction mixture was cooled to r.t. and treated with an aqueous solution (25 ml) of NH₄PF₆ (165 mg, 1.01 mmol). The resulting dark coloured precipitate was collected by filtration, washed with H₂O followed by Et₂O and dried *in vacuo*. The solids were recrystallised from CH₂Cl₂ / hexanes giving the title complex as a dark brown powder. Yield = 347 mg, 80 %. ¹H NMR (d₃-MeCN, 400 MHz): 5.37 (s, 8H), 7.15 (d, *J* = 7.3 Hz, 8H), 7.28-7.41 (m, 12H), 8.66 (s, 4H), 9.28 (s, 4H). ¹³C NMR (d₃-MeCN, 101 MHz): 56.73, 127.70, 129.42, 130.10, 130.18, 133.84, 140.57, 145.78, 149.48. HRMS (ES); *m/z* calc. for [C₄₄H₃₆N₁₆Os]²⁺: 490.1456 (M²⁺), found: 490.1457. Anal. Cal'd. for C₄₄H₃₆N₁₆P₂F₁₂Os (%): C 41.64, H 2.86, N 17.66, found (%): C 41.77, H 2.67, N 17.76.

Synthesis of Os3

[(NH₄)₂OsCl₆] (150 mg, 0.34 mmol) and **7** (225 mg, 0.72 mmol) were combined in ethylene glycol (25 ml) and heated to reflux for 16 h. The reaction mixture was cooled to r.t. and treated with an aqueous solution (25 ml) of NH₄PF₆ (275 mg, 1.69 mmol). The resulting dark green coloured precipitate was collected by filtration, washed with H₂O and dried *in vacuo*. The solids were purified by column chromatography (Al₂O₃, 4:1 CH₂Cl₂ / MeCN) followed by recrystallisation from MeCN / Et₂O, giving the desired complex as a dark green powder. Yield = 100 mg, 27 %. ¹H NMR (d₃-MeCN, 400 MHz): 5.33 (s, 4H), 7.06-7.13 (m, 6H), 7.23 (d, *J* = 5.5 Hz, 2H), 7.26-7.38 (m, 6 H), 7.76 (td, *J* = 1.5, 7.8 Hz, 2H), 7.87 (t, *J* = 8.0 Hz, 2H), 8.34 (d, *J* = 8.0 Hz, 2H), 8.39 (d, *J* = 8.0 Hz, 2H), 8.55 (s, 2H), 8.56 (d, *J* = 8.0 Hz, 2H). ¹³C NMR (d₃-MeCN, 101 MHz): 56.44, 121.44, 121.73, 125.40, 127.20, 128.51, 129.21, 130.00, 130.02, 134.15, 136.94, 138.53, 150.99, 151.97, 153.30, 156.92, 161.11. HRMS (ES); *m/z* calc. for [C₃₈H₃₀N₁₀Os]²⁺: 409.1129 (M²⁺), found:

409.1148. Anal. Calc'd for $C_{38}H_{30}N_{10}P_2F_{12}Os$ (%): C 41.23, H 2.73, N 12.65, found (%): C 41.20, H 2.69, N 12.57.

Synthesis of Os4

$[(NH_4)_2OsCl_6]$ (153 mg, 0.35 mmol) and **10** (236 mg, 0.75 mmol) were combined in ethylene glycol (20 ml) and heated to reflux for 17 h. The reaction mixture was cooled to r.t. and treated with an aqueous solution (10 ml) of NH_4PF_6 (337 mg, 2.06 mmol). The resulting dark green precipitate was collected by filtration, washed with H_2O followed by Et_2O and dried *in vacuo*. The solids were purified by column chromatography (SiO_2 , 1:1:10 (v/v/v) H_2O / sat. aq. KNO_3 / MeCN), which after subsequent counter-ion metathesis gave the title complex as a dark green powder. Yield = 172 mg, 45 %. 1H NMR (d_3 -MeCN, 400 MHz): 5.35 (s, 4H), 7.08-7.21 (m, 6H), 7.23-7.40 (m, 8H), 7.86 (t, $J = 7.6$ Hz, 2H), 8.57 (d, $J = 7.9$ Hz, 2H), 8.66 (s, 2H), 9.38 (s, 2H), 9.64 (s, 2H). ^{13}C NMR (d_3 -MeCN, 101 MHz): 56.68, 125.86, 127.65, 128.75, 129.39, 130.02, 130.09, 133.80, 139.64, 141.94, 142.62, 144.63, 149.05, 150.41, 154.40, 158.59. HRMS (ES); m/z calc. for $[C_{36}H_{28}N_{12}Os]^{2+}$: 410.1082 (M^{2+}), found: 410.1090. Anal. Calc'd for $C_{36}H_{28}N_{12}OsP_2F_{12}$ (%): C 38.99, H 2.55, N 15.16, found (%): C 38.88, H 2.60, N 15.03.

Synthesis of Os5

$[(NH_4)_2OsCl_6]$ (62 mg, 0.14 mmol) and **14** (90 mg, 0.29 mmol) were combined in ethylene glycol (8 ml) and heated to reflux for 7 h. The reaction mixture was cooled to r.t. and treated with an aqueous solution (8 ml) of NH_4PF_6 (112 mg, 0.69 mmol). The resulting precipitate was collected by filtration, washed with H_2O followed by Et_2O and dried *in vacuo*. The solids were subsequently re-dissolved in MeCN (12 ml), refrigerated for 5 h and then passed quickly through a short (2 cm) celite pad. Addition of excess Et_2O to the filtrate re-precipitated a dark green powder which was purified further by column chromatography (Al_2O_3 , 1:1:10 (v/v/v) H_2O / sat. aq. KNO_3 / MeCN). Subsequent counter-ion metathesis furnished the desired complex as dark green solids. Yield = 93 mg, 60 %. 1H NMR (d_3 -MeCN, 400 MHz): 5.35 (s, 4H), 7.14 (d, $J = 7.1$ Hz, 4H), 7.28-7.40 (m, 8H), 7.98 (t, $J = 8.2$ Hz, 2H), 8.11 (d, $J = 3.3$ Hz, 2H), 8.42 (d, $J = 8.0$ Hz, 2H), 8.58 (s, 2H), 8.72 (d, $J = 8.1$ Hz, 2H), 9.50 (d, $J = 0.5$ Hz, 2H). ^{13}C NMR (d_3 -MeCN, 101 MHz): 56.60, 121.83, 121.99, 127.54, 129.42, 130.02, 130.09, 133.83, 138.28, 145.88, 147.53, 149.78, 151.32, 151.75, 155.66, 156.93. HRMS (ES); m/z calc. for $[C_{36}H_{28}N_{12}Os]^{2+}$: 410.1082 (M^{2+}), found: 410.1104; m/z calc. for

$[\text{C}_{36}\text{H}_{28}\text{N}_{12}\text{PF}_6\text{Os}]^{2+}$: 965.1817 (M^+), found: 965.1825. Anal. Calc'd for $\text{C}_{36}\text{H}_{28}\text{N}_{12}\text{OsP}_2\text{F}_{12}$ (%): C 38.99, H 2.55, N 15.16, found (%): C 38.80, H 2.46, N 15.04.

Synthesis of Os6

$[(\text{NH}_4)_2\text{OsCl}_6]$ (77 mg, 0.17 mmol) and **17** (114 mg, 0.36 mmol) were combined in ethylene glycol (10 ml) and heated to reflux for 7 h. The reaction mixture was cooled to r.t. and treated with an aqueous solution (10 ml) of NH_4PF_6 (146 mg, 0.89 mmol). The resulting precipitate was collected by filtration, washed with H_2O followed by Et_2O and dried *in vacuo*. Purification was carried out by column chromatography (SiO_2 , 0.06:1:1:10 (v/v/v/v) Et_3N / H_2O / sat. aq. KNO_3 / MeCN) which, after counter-ion metathesis, afforded the product as a dark green solid. Yield = 58 mg, 30 %. ^1H NMR (d_3 - MeCN , 400 MHz): 5.36 (s, 4H), 7.16 (d, J = 6.9 Hz, 4H), 7.29-7.40 (m, 6H), 7.45 (d, J = 3.2 Hz, 2H), 8.21 (d, J = 3.3 Hz, 2H), 8.73 (s, 2H), 9.46 (s, 2H), 9.69 (s, 2H), 9.81 (s, 2H). ^{13}C NMR (d_3 - MeCN , 101 MHz): 56.85, 128.08, 129.58, 130.05, 130.19, 133.54, 142.36, 142.79, 145.12, 146.30, 148.67, 148.94, 149.50, 150.02, 154.38. HRMS (ES); m/z calc. for $[\text{C}_{34}\text{H}_{26}\text{N}_{14}\text{Os}]^{2+}$: 411.1034 (M^{2+}), found: 411.1044. Anal calc'd for $\text{C}_{34}\text{H}_{26}\text{N}_{14}\text{OsP}_2\text{F}_{12}$ (%): C 36.76, H 2.36, N 17.65, found (%): C 36.89, H 2.44, N 17.83.

Computational Details

The ground state geometries of the complexes were optimised in the gas phase at the B3LYP level of theory⁶⁴ using the Stuttgart-Dresden relativistic small core effective core potential⁶⁵ and basis set for osmium and 6-311G* basis sets⁶⁶ for all other atoms using the NWChem software package.⁶⁷ Molecular orbital energies and isosurface plots were then calculated in single-point calculations at the same level of theory using the SMD solvation model (acetonitrile).⁶⁸ HOMO and LUMO plots were produced using the Gabedit⁶⁹ viewer software. TDDFT calculations were also carried out including the solvation model with the first 50 singlet and 10 triplet roots determined.

Associated Content

Supporting Information is available free of charge on the ACS publications website at DOI:

NMR spectroscopy and mass spectrometry characterisation data, additional electrochemical data, low temperature (77 K) photoluminescence spectra, optimised geometry coordinates for **Os1-Os7** and calculated UV-Visible absorption spectra for **Os1-Os6**.

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Notes

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TOC Entry:

Observation of an inversion in photophysical tuning in a systematic study of luminescent triazole-based osmium(II) complexes

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A systematic survey of a series of bis(terdentate) Os(II) complexes captures the tipping-point at which inversion of photophysical properties through ligand-based tuning occurs upon increasing π -accepting ligand character.