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Substituent directed selectivity in anion recognition by a new class of simple osmium-pyrazole derived receptor

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†Electronic supplementary information (ESI) available: X-ray crystallographic file for [**1**]ClO_4 and [**2**]ClO_4 in CIF format, mass spectra (Figs. S1, S9), Mulliken spin density (Fig. S2), colorimetry (Fig. S3), pK_a plot (Fig. S4), UV-vis plots (Fig. S5), NMR (Figs. S6-S8), log *K* plots (Fig. S10), DFT optimised structures (Figs. S11-S12), bond parameters (Tables S1-S2) and DFT data (Tables S3-S13). CCDC nos. 1430164 ([**1**]ClO_4), 1430165 ([**2**]ClO_4).

Abstract

The present article deals with the structurally, spectroscopically and electrochemically characterised osmium-bipyridyl derived complexes $[(bpy)_2Os^{II}(HL_1)Cl]ClO_4$ [**1**]ClO_4 and $[(bpy)_2Os^{II}(HL_2)Cl]ClO_4$ [**2**]ClO_4 incorporating neutral and monodentate pyrazole derivatives (HL) with one free NH function (bpy = 2,2′-bipyridine, HL_1 = pyrazole, HL_2 = 3,5-dimethylpyrazole). The crystal structures of [**1**]ClO_4 and [**2**]ClO_4 reveal intramolecular hydrogen bonding interaction between the free NH proton of HL and the equatorially placed Cl^- ligand (N-H···Cl) with donor-acceptor distances of 3.114(7) Å and 3.153(6) Å as well as intermolecular hydrogen bonding interaction between the NH proton and one of the oxygen atoms of ClO_4^- (N-H···O) with donor-acceptor distances of 2.870(10) Å and 3.024(8) Å, respectively. The effect of hydrogen bonding interactions has translated into the less acidic nature of the NH proton of the coordinated HL with estimated pK_a>12. $\mathbf{1}^+$ and $\mathbf{2}^+$ exhibit reversible Os(II)/(III) and irreversible Os(III)/(IV) processes in CH_3CN within ± 2.0 V *versus* SCE. The effect of 3,5-dimethyl substituted HL_2 in $\mathbf{2}^+$ has been reflected in the appreciable lowering (40 mV) of $Os^{II/III}$ potential, along with further decrease in acidity of the NH proton (pK_a>13.0) with regard to HL_1 coordinated $\mathbf{1}^+$ (pK_a: ~12.3). The electronic spectral features of Os(II) ($\mathbf{1}^+$/$\mathbf{2}^+$) and electrochemically generated Os(III) ($\mathbf{1}^{2+}$/$\mathbf{2}^{2+}$) derived complexes have been analysed by TD-DFT calculations. The efficacy of $\mathbf{1}^+$ and $\mathbf{2}^+$ encompassing free NH proton towards the anion recognition process has been evaluated by different experimental investigations using a wide variety of anions. It however establishes that receptor $\mathbf{1}^+$ can recognise both F^- and OAc^- in acetonitrile solution, while $\mathbf{2}^+$ is exclusively selective for the F^- ion.

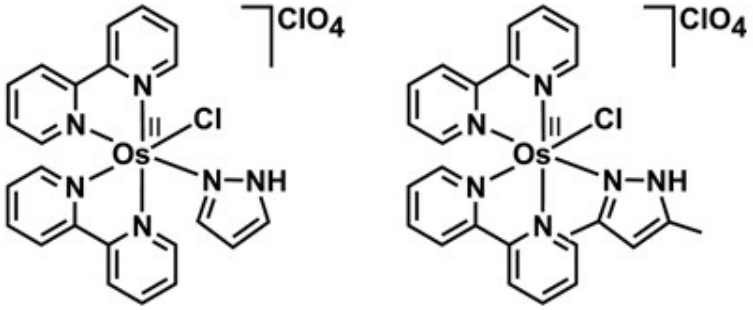
Introduction

Selective recognition of anion(s) by suitably designed receptor is an important chemical event since anions play vital roles in various chemical, biological and environmental processes.[1] A wide variety of receptors for the anion recognition process in aprotic solvents, involving hydrogen bonding interaction and Bronsted acid-base chemistry is well documented in literature.[2] One of the commonly adopted approaches towards the fabrication of effective receptor for the anion sensing process includes the development of metal complex framework encompassing one or more ligands embedded with free NH function(s).[3] The complex mode of non-covalent interactions between the receptor and anion could however be efficiently monitored by different experimental techniques in combination with theoretical insights.[4] The strong metal-ligand charge transfer transition in the lower energy visible region as well as facile electron-transfer process within the accessible solvent potential window make the transition metal derived receptors rather attractive[5] as compared to otherwise popular organic based receptors such as urea, thiourea, imidazole ion, amide, phenol.[2*d*,3*c*,5]

In this regard, ruthenium-polypyridyl (2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), 2,2′:6′,2′-terpyridine (trpy)) derived frameworks incorporating active ligands with free NH proton(s) have been established as effective receptors for selective anions.[6] The examples of analogous osmium based complexes as possible receptor for selected anion(s) are however limited to a few recent reports.[6*f*-*g*,7]

This indeed is the genesis of the present article demonstrating structural and spectroelectrochemical aspects of two newly designed osmium-bipyridine derived complexes $[(bpy)_2Os^{II}(HL_1)Cl]ClO_4$ [**1**]ClO_4 and $[(bpy)_2Os^{II}(HL_2)Cl]ClO_4$ [**2**]ClO_4 (Scheme 1) involving pyrazole derivatives, HL_1 = pyrazole, HL_2 = 3,5-dimethylpyrazole with one free NH proton of

varying acidity. The present exploration with a series of anions such as F^-, Cl^-, Br^-, I^-, OAc^-, SCN^-, NO_3^-, HSO_4^-, $H_2PO_4^-$ *via* the combination of different experimental techniques and DFT calculations has revealed a unique feature of $\mathbf{2}^+$ in contrast to $\mathbf{1}^+$ towards the selective recognition of F^- ion.



[**1**]ClO_4 [**2**]ClO_4

Scheme 1 Representation of complexes.

Though pyrazole derived osmium systems are available in literature,[8] to the best of our knowledge the present article demonstrates for the first time the use of the osmium-pyrazoles, $\mathbf{1}^+$ and $\mathbf{2}^+$ towards the recognition of anions with special reference to the remarkable impact of substituent (H ($\mathbf{1}^+$) *versus* Me ($\mathbf{2}^+$)) on the exclusive selectivity process.[9]

Results and discussion

Synthesis, general characterisation and crystal structures

The mononuclear complexes $[(bpy)_2Os^{II}(HL_1)Cl]ClO_4$, [**1**]$ClO_4$ and $[(bpy)_2Os^{II}(HL_2)Cl]ClO_4$, [**2**]$ClO_4$ (bpy = 2,2′-bipyridine, HL_1 = pyrazole, HL_2 = 3,5-dimethylpyrazole) have been synthesised in fairly good yield from the precursor complex *cis*-$[Os^{II}(bpy)_2(Cl)_2]$ and HL_1 or HL_2, in refluxing 1:1 ethanol-water under dinitrogen atmosphere followed by precipitation using saturated aqueous $NaClO_4$ solution. The complexes have been purified by column chromatography on a neutral alumina column (Experimental).

The complexes have been characterised by their satisfactory microanalytical data, molar conductivity and mass spectrometry (Fig. S1† and Experimental). The IR spectrum as KBr disc of [**1**]ClO_4 or [**2**]ClO_4 displays $\nu(ClO_4)$ vibrations around 1100 cm^{-1} and 625 cm^{-1},[10] however, NH vibration of coordinated HL_1 or HL_2 has not been clearly resolved primarily due to the appearance of a broad OH vibration around 3400 cm^{-1}.

The crystal structures of [**1**]ClO_4 and [**2**]ClO_4 are shown in Figs. 1, 2 and selected crystallographic and bond parameters are set in Tables 1, 2 and S1, S2†, respectively. The crystal structure establishes that the ligand HL_1 or HL_2 binds to the metal ion by its neutral N donor leaving the free NH proton accessible for further chemical reactivity (see later). The distorted octahedral geometry around the osmium ion in [**1**]ClO_4/[**2**]ClO_4 has been corroborated by the smaller *trans* angles, N1-Os1-N5 = 174.2(3)°/177.3(3)°, N3-Os1-N6 = 176.0(3)°/177.7(2)°, N4-Os1-Cl1 = 174.4(2)°/173.70(19)° and bite angles N3-Os1-N4 = 78.7(3)°/78.0(2)°, N5-Os1-N6 = 79.2(3)°/78.3(2)°, N1-Os1-Cl=90.0(2)°/87.66(17)°. The average Os^{II}-N(bpy),[7f-g,11] Os^{II}-N(HL)[8b,12] and Os^{II}-Cl[8b,12a-b,13] bond lengths in [**1**]ClO_4/[**2**]ClO_4 of 2.043(7)/2.039(7) Å,

2.106(7)/2.104(6) Å and 2.430(2)/2.407(2) Å, respectively, match well with the reported corresponding distances in analogous complexes.

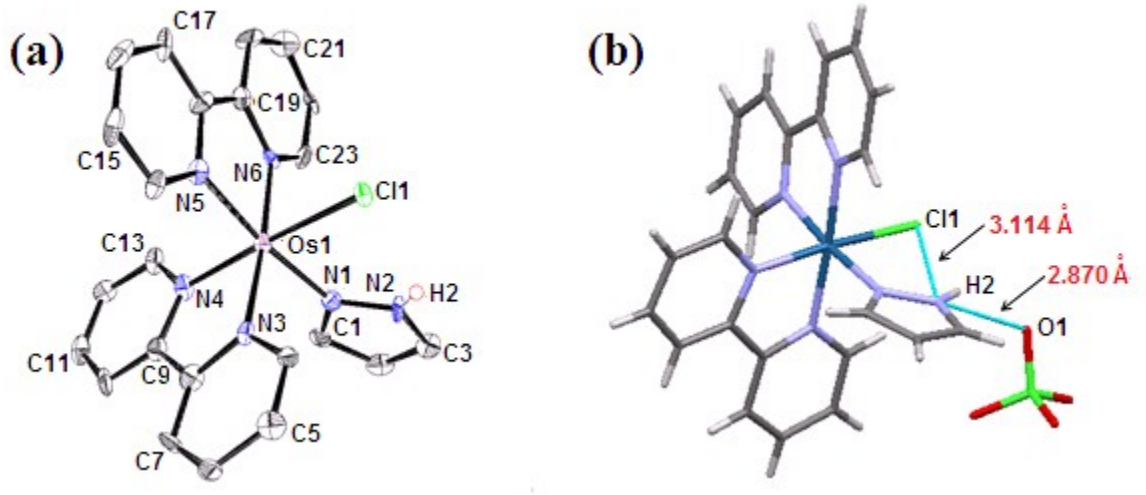


Fig. 1 (a) ORTEP diagram of the cationic part of [**1**]ClO_4. Ellipsoids are drawn at the 40% probability level. Hydrogen atoms (C-H) are omitted for clarity. (b) Perspective view showing the intramolecular N-H···Cl and intermolecular N-H···O hydrogen bonding interactions.

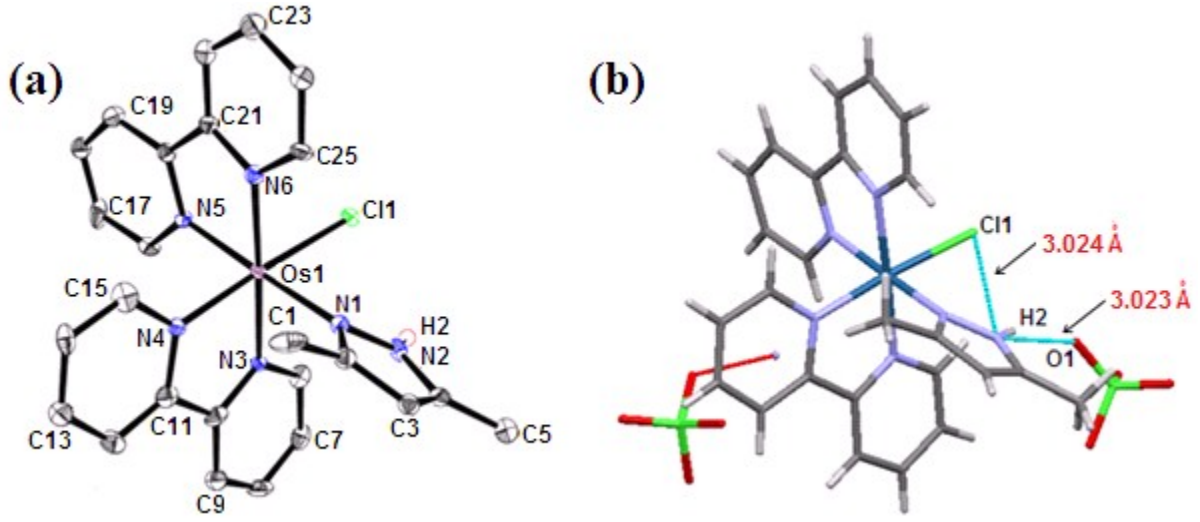


Fig. 2 (a) ORTEP diagram of the cationic part of [**2**]ClO_4. Ellipsoids are drawn at the 40% probability level. Hydrogen atoms (C-H) are omitted for clarity. (b) Perspective view showing the intramolecular N-H···Cl and intermolecular N-H···O hydrogen bonding interactions.

Table 1 Selected crystallographic parameters of [**1**]ClO_4 and [**2**]ClO_4

Compound	[**1**]ClO_4	[**2**]ClO_4
Formula	$C_{23}H_{20}N_6O_4Cl_2Os$	$C_{25}H_{24}N_6O_4Cl_2Os$
M_r	705.55	733.60
Radiation	MoKα	MoKα
Crystal system	orthorhombic	Monoclinic
Space group	*Pbca*	P_12_1/n_1
a /Å	26.520(8)	15.017(8)
b /Å	13.627(4)	11.932(5)
c /Å	13.432(4)	15.605(8)
α (°)	90	90
β (°)	90	113.401(6)
γ (°)	90	90
V /Å^3	4854(3)	2566(2)
Z	8	4
μ /mm^{-1}	5.518	5.223
T /K	100(2)	100(2)
ρ_{calcd} /g cm^{-3}	1.931	1.899
F(000)	2736	1432
θ range(°)	3.073 to 25.242	3.139 to 25.00
Data/ restraints/ parameters	4253/0/325	4507/78/345
R_1, wR_2 [$I > 2\sigma(I)$]	0.0582, 0.0904	0.0499, 0.0985
R_1, wR_2 (all data)	0.0656, 0.0931	0.0640, 0.1048
GOF on F^2	1.246	1.133
Largest diff. peak per hole /e Å^{-3}	0.949/-0.945	1.631/-1.463

Table 2 Experimental and DFT calculated selected bond distances (Å) of [**1**]ClO_4 and [**2**]ClO_4

	[**1**]ClO_4		[**2**]ClO_4	
Bond distances (Å)	X-ray	DFT	X-ray	DFT
Os1-N1	2.106(7)	2.139	2.104(6)	2.165
Os1-N3	2.060(7)	2.087	2.058(7)	2.088
Os1-N4	2.024(7)	2.054	2.020(6)	2.051
Os1-N5	2.044(7)	2.065	2.035(6)	2.066
Os1-N6	2.045(7)	2.077	2.044(7)	2.076
Os1-Cl1	2.430(2)	2.481	2.407(2)	2.486
N1-C1	1.333(10)	1.343	-	-
N1-C2	-	-	1.341(9)	1.351
C1-C2	1.401(12)	1.403	1.504(10)	1.497
C2-C3	1.368(13)	1.386	1.392(10)	1.407
N2-C3	1.353(10)	1.348	-	-
N1-N2	1.342(9)	1.351	1.374(8)	1.361
N2-C4	-	-	1.335(9)	1.350
C3-C4	-	-	1.361(10)	1.387
C4-C5	-	-	1.496(10)	1.495
N2-Cl1	3.114(7)	3.050	3.153(6)	3.032
N2-O1	2.870(10)	-	3.024(8)	-

The appreciably longer Os^{II}-N(HL) distance with respect to the Os^{II}-N(bpy) distance in [**1**]ClO_4 or [**2**]ClO_4 is a reflection of the weak π-accepting feature of HL as compared to bpy.[14] The π-donating ability of Cl^- has resulted in the shortest Os^{II}-N4(bpy) distance (N4 *trans* to Cl^-) due to the enhanced back bonding effect as compared to the rest of the Os^{II}-N(bpy) distances.

The crystal structure of [**1**]ClO_4 or [**2**]ClO_4 also confirms the presence of intramolecular as well as intermolecular hydrogen bonding interactions.[12*a*,15] The intramolecular hydrogen bonding in [**1**]ClO_4 or [**2**]ClO_4 takes place between the free NH protons associated with HL and the equatorially positioned Cl^- with the donor acceptor distance/angle, N2-Cl1/N2-H2···Cl1 of 3.112 Å/123.8^0 or 3.153 Å/114.9^0, respectively. The intermolecular hydrogen bonding in [**1**]ClO_4 involves NH proton of the coordinated HL_1 ligand and one of the oxygen atoms (O1) of the

perchlorate counter anion in the asymmetric unit with N2···O1 distance and N2-H2···O1angle of 2.870 Å and 136.5^0, respectively. However, the same in [**2**]ClO_4 is associated with the NH proton of HL_2 in one asymmetric unit and one of the oxygen atoms (O1) of perchlorate in the nearby asymmetric unit which results in N2-O1 distance of 3.023 Å and N2-H2···O1 angle of 155.9^0.

^{1}H-NMR spectrum of the diamagnetic [**1**]ClO_4 in $(CD_3)_2SO$ exhibits partially overlapping 16 bpy and 3 CH proton resonances for HL_1 in the chemical shift region δ, 6-10 ppm in addition to one NH signal of HL_1 at δ, 12.83 ppm (Fig. 3 and Experimental). Though two CH protons of HL_1 are clearly observable at δ, 6.79 ppm and 6.29 ppm, the third CH proton is being merged with the bpy resonance at δ, 7.08 ppm. The ^{1}H-NMR of [**2**]ClO_4 in $(CD_3)_2SO$ displays 16 partially overlapping bpy proton resonances in the chemical shift region of δ, 6.5-10 ppm and

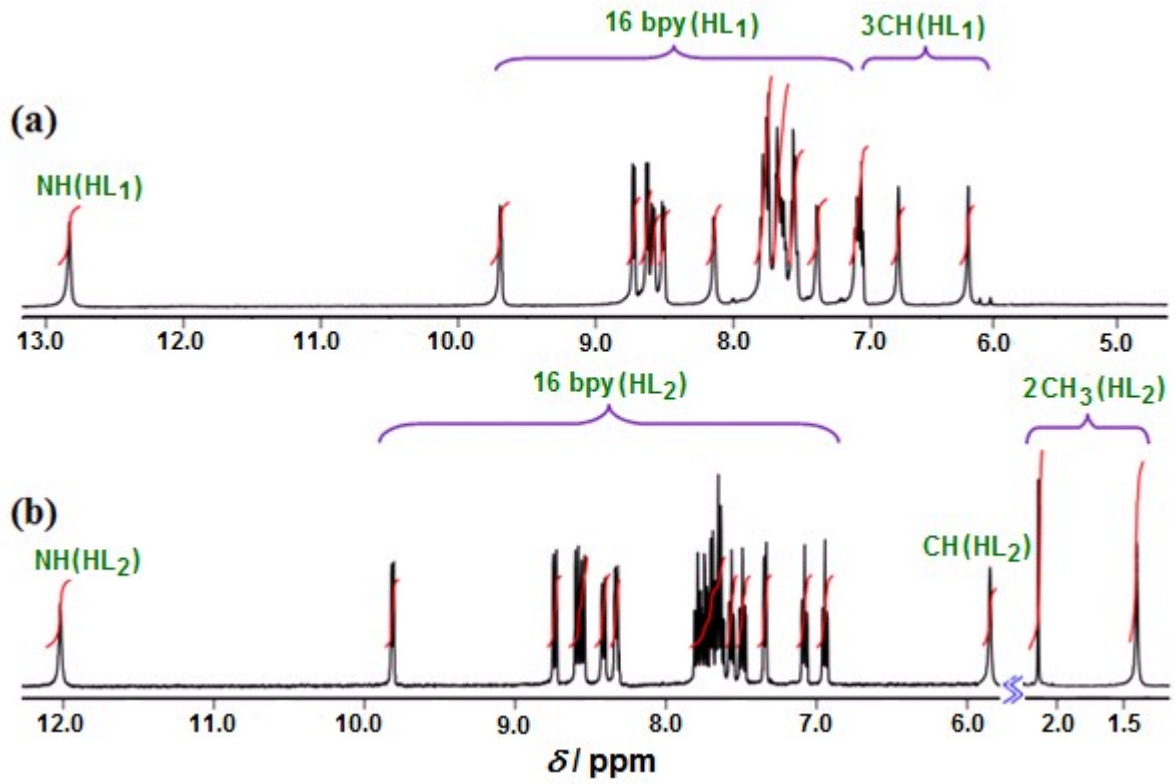


Fig. 3 ^{1}H-NMR spectra of (a) [**1**]ClO_4 and (b) [**2**]ClO_4 in $(CD_3)_2SO$.

three singlets corresponding to CH proton and $2CH_3$ groups of HL_2 at δ, 5.84 and 2.18, 1.29 ppm, respectively. The impact of the two electron donating CH_3 groups of HL_2 in $\mathbf{2}^+$ in relation to HL_1 in $\mathbf{1}^+$ has been reflected in the upfield shifted less acidic NH proton resonance for the former (δ, 12.01 ppm) as compared to the latter (δ, 12.83 ppm). Furthermore, the presence of intramolecular N-H···Cl and intermolecular N-H···O hydrogen bonding interactions between the NH proton of HL and Cl/oxygen atom of ClO_4^- counter anion, respectively, in both [**1**]ClO_4 and [**2**]ClO_4 as revealed by their crystal structures (Figs. 1, 2) causes the NH proton of the complexes to appear at the down field region[16] as compared to that of the free pyrazole moiety (δ, 11.90 ppm).

Spectroelectrochemical features

The complexes $\mathbf{1}^+$ and $\mathbf{2}^+$ display reversible one oxidation (Ox1) and one reduction (Red1) processes with $E_{298}{}^0$,V at ~ 0.30 V and ~ –1.70 V, respectively in CH_3CN *versus* SCE (Fig. 4, Table 3). The cathodic shift of 40 mV of Ox1 has taken place while moving from $\mathbf{1}^+$ to $\mathbf{2}^+$ due to

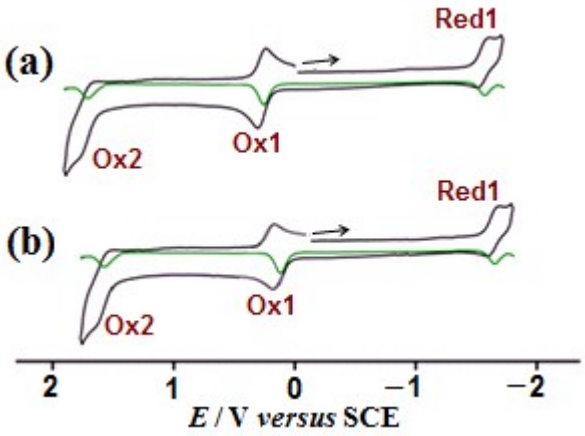


Fig. 4 Cyclic (black) and differential pulse (green) voltammograms in CH_3CN/0.1 M $NEt_4{}^+ClO_4^-$ for (a) [**1**]ClO_4 and (b) [**2**]ClO_4.

Table 3 Electrochemical data[a]

Complex	$E°_{298}$ /V (ΔE_p/mV)[b]			Reference
	Ox2	Ox1	Red1	
$[(bpy)_2Os^{II}(HL_1)Cl]^+$	1.70(100)	0.32(60)	-1.69(90)	This work
$[(bpy)_2Os^{II}(HL_2)Cl]^+$	1.57(110)	0.28(60)	-1.71(100)	This work
$[(bpy)_2Ru^{II}(HL_1)Cl]^+$	-	0.81	-	17
$[(bpy)_2Ru^{II}(HL_2)Cl]^+$	-	0.79	-	17

[a]From cyclic voltammetry in CH_3CN/0.1 M Et_4NClO_4 at 100 mV s^{-1}.

[b]Potentials in V *versus* SCE; peak potential differences ΔE_p in parentheses.

the impact of electronic donating two CH_3 groups in the framework of HL_2. $\mathbf{1}^+$ or $\mathbf{2}^+$ also exhibits an irreversible second oxidation (Ox2) at around 1.6 V.

The primary involvements of Os (Os^{II}/Os^{III} (Ox1) and $Os^{III}\rightarrow Os^{IV}$ (Ox2) and bpy (Red1) based orbitals in the redox processes of $\mathbf{1}^n$ or $\mathbf{2}^n$ have been realised by the DFT calculated MO compositions (Tables S3-S11†) and Mulliken spin density distributions at the paramagnetic intermediates (Fig. S2†, Table S12†). The partial contribution of HL/Cl in the MOs and spin distributions in $\mathbf{1}^n$ or $\mathbf{2}^n$ can be attributed to the effect of metal-ligand covalency.[14*a*-*b*,18] The electrochemically generated paramagnetic $\mathbf{1}^{2+}$ or $\mathbf{2}^{2+}$ (S=1/2) has however failed to show the expected EPR signal even at 77 K, due to the rapid relaxation process (~10^{-8} s) *via* the strong spin orbit coupling effect of heavier Os^{III} ion (λ=3000 cm^{-1}).[19]

The significantly lower Os^{II}/Os^{III} potential of $\mathbf{1}^+$ or $\mathbf{2}^+$ as compared to that of the reported analogous $[Ru^{II}(bpy)_2(HL)]^+$ (0.8 V, Table 3) implies the relatively higher stability of the Os(III) over the Ru(III) state primarily due to the stronger π-donor feature of Os(II).[7*g*,14*a*,20]

The change in electronic spectral profiles of $\mathbf{1}^+$ and $\mathbf{2}^+$ on reversible oxidation to $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$, respectively, has been shown in Fig. 5 and Table S13†. $\mathbf{1}^+$ and $\mathbf{2}^+$ exhibit similar spectral profile

with multiple bands in the UV-vis region in CH_3CN.[7g,14a,19b,21] The origin of transitions has been evaluated by TD-DFT calculations. The moderately intense lowest energy bands at 724 nm and 734 nm for $\mathbf{1}^+$ and $\mathbf{2}^+$ are predicted to be originated *via* the (dπ)Os/(π)Cl→(π*)bpy and (dπ)Os/(π)bpy→(π*)bpy derived MLLCT (metal/ligand to ligand charge transfer) transitions, respectively. The other two intense visible bands at around 520 nm and 430 nm for $\mathbf{1}^+$ or $\mathbf{2}^+$ are however of the same origin of (dπ)Os/(π)bpy→(π*)bpy. On oxidation of $\mathbf{1}^+$ to $\mathbf{1}^{2+}$ or $\mathbf{2}^+$ to $\mathbf{2}^{2+}$, the lowest energy band around 700 nm of $\mathbf{1}^+/\mathbf{2}^+$ disappears completely and the visible bands of $\mathbf{1}^+/\mathbf{2}^+$ around 500 nm undergo slight blue shifting with the significant reduction in intensity, which are

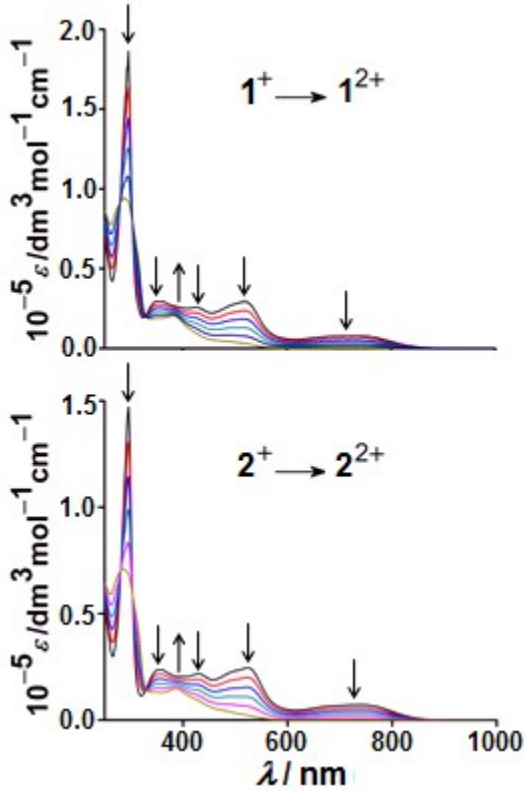


Fig. 5 Spectroelctrochemical plots for $\mathbf{1}^+ \rightarrow \mathbf{1}^{2+}$ and $\mathbf{2}^+ \rightarrow \mathbf{2}^{2+}$ in CH_3CN.

assigned to (π)HL/(π)bpy→(dπ)Os, (π)bpy→(dπ)Os and (π)HL→(dπ)Os based LLMCT (ligand/ligand to metal charge transfer) and LMCT (ligand to metal charge transfer) transitions.[7g,11]

Anion binding aspects of $\mathbf{1}^+$ and $\mathbf{2}^+$

The effectivity of $\mathbf{1}^+$ or $\mathbf{2}^+$ encompassing one hydrogen bonded NH proton in the framework of coordinated HL, as a receptor for the selective interaction with anion(s) has been explored by a series of experimental and DFT calculations.

In this regard, the initial assessment has been made by monitoring the change in colour of $\mathbf{1}^+$ and $\mathbf{2}^+$ on addition of tetrabutylammonium salts of F^-, Cl^-, Br^-, I^-, OAc^-, SCN^-, NO_3^-, HSO_4^-, $H_2PO_4^-$. The introduction of F^-/OAc^- and F^- (two equivalents) to the acetonitrile solution of $\mathbf{1}^+$ and $\mathbf{2}^+$, respectively, has marked a distinct change in colour from brown to violet. However, the colour of $\mathbf{1}^+$ and $\mathbf{2}^+$ remains unaltered even up to the addition of 8 equivalents of Cl^-, Br^-, I^-, SCN^-, NO_3^-, HSO_4^- and $H_2PO_4^-$ (Fig. S3†). The colorimetric experiment thus extends an immediate impression of varying selectivity patterns of $\mathbf{1}^+$ and $\mathbf{2}^+$ towards the tested set of anions which indeed has prompted us to cross examine the anion selectivity features by the following spectroscopic, ITC (Isothermal Titration Calorimetry) and electrochemical techniques.

In agreement to the colorimetric experiment in Fig. S3†, the spectral profile of $\mathbf{1}^+$ or $\mathbf{2}^+$ has failed to change on addition of up to 8 equivalents of Cl^-, Br^-, I^-, NO_3^-, SCN^-, $H_2PO_4^-$ and HSO_4^- (Fig. 6). However, the gradual additions of F^-/OAc^- and F^- up to 2 equivalents in $\mathbf{1}^+$ and $\mathbf{2}^+$ have established the shift of MLCT bands at 520 nm to 545 nm/520 nm to 540 nm and 524 nm to 543 nm, respectively, with a sharp change in colour from brown to violet and no further change in band position or intensity is observed thereafter (up to 8 equivalents (Fig. 6)), implying the selectivity of F^-/OAc^- for the former and F^- selectivity for the latter. The relatively lower acidity of the NH proton of $\mathbf{2}^+$ (pK_a of $\mathbf{1}^+$: ~12.3; pK_a of $\mathbf{2}^+$ > 13.0 (beyond the scope of instrumental detection, Fig. S4†) due to the impact of electron releasing two methyl groups in the framework of HL_2 can account for this observed exclusive selectivity of $\mathbf{2}^+$ for F^- in contrast to

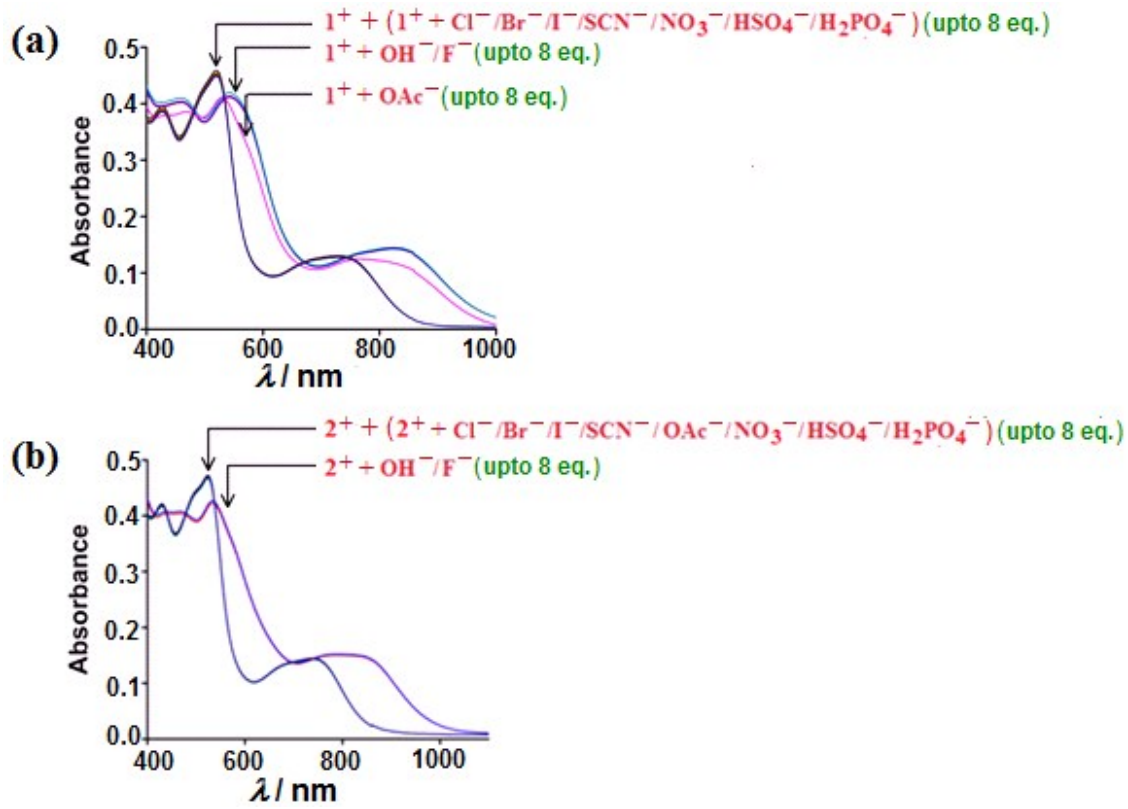


Fig. 6 UV-vis spectral changes in CH_3CN on addition of eight equivalents of the TBA salt of anions in (a) $\mathbf{1}^+$ and (b) $\mathbf{2}^+$ ($5x10^{-5}$ mol dm^{-3}).

F^- and OAc^- for $\mathbf{1}^+$. The deprotonation of HL in $\mathbf{1}^+$ or $\mathbf{2}^+$ *via* the selective interaction with F^- or OAc^- has been corroborated by the identical spectral changes in presence of one equivalent stronger base OH^- (Fig. 7). The deprotonated **1** and **2** can quantitatively be reconverted to $\mathbf{1}^+$ and $\mathbf{2}^+$, respectively, in the presence of H_2O as a proton source.

The sequential transformation of $\mathbf{1}^+/\mathbf{2}^+$ to the deprotonated state of **1**/**2** in the presence of F^- proceeds through clean isosbestic points (Figs. 7 and S5†). The observed spectral saturation with two equivalents of F^- suggests 1:2 stoichiometry between the receptor and the interacting anion.[1n,2d,4d,22] However, the requirement of excess equivalents of anion (2 equivalents) for the monodeprotonation process can be attributed to the fact of the weak acidic feature of the NH proton due to its strong intramolecular and intermolecular hydrogen bonding interactions

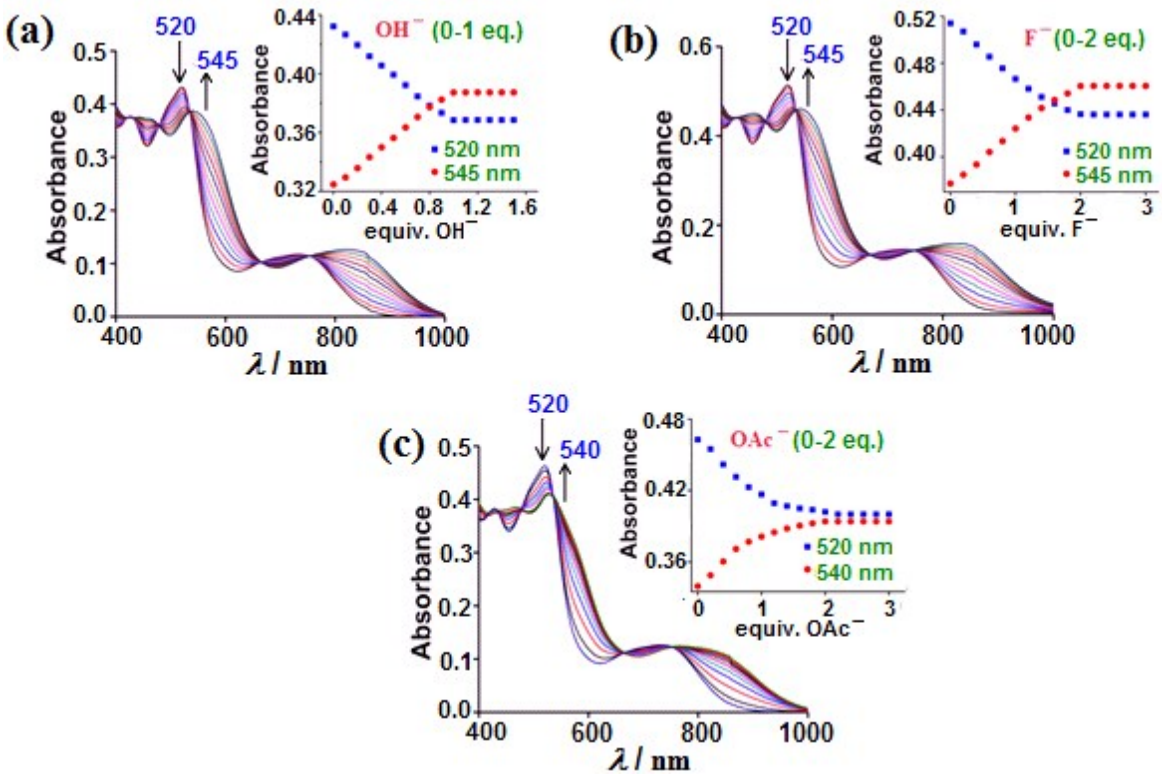


Fig. 7 UV-vis spectral changes of $\mathbf{1}^+$ ($5x10^{-5}$ mol dm^{-3}) in CH_3CN on gradual additions of (a) OH^-, (b) F^- and (c) OAc^-. The inset shows the changes in absorbances at 520 nm, 545 nm for OH^- and F^-; 520 nm and 540 nm for OAc^- as a function of the equivalents of respective anions.

with the equatorially placed Cl^- ligand and perchlorate anion, respectively, as evidenced by the crystal structures of [**1**]ClO_4 and [**2**]ClO_4 (Figs. 1, 2).

The interaction profile of $\mathbf{1}^+$ and $\mathbf{2}^+$ with F^- was further investigated by ^{1}H-NMR and ^{19}F-NMR titration in $(CD_3)_2SO$. The gradual addition of TBAF up to one equivalent (Figs.8 and S6†) to the solution of $\mathbf{1}^+$ or $\mathbf{2}^+$, results in broadening of the NH proton signal at δ, 12.83 ppm ($\mathbf{1}^+$) or 12.01 ppm ($\mathbf{2}^+$) followed by its disappearance, possibly due to initial hydrogen bonding interaction with the anion,[4b,d,23] ultimately causing proton abstraction. Moreover, the incremental addition of the anion, up to two equivalents lead to the emergence of a new broad signal (triplet) at around δ, 16 ppm corresponding to HF_2^-.[24] The effect of anion (up to two equivalents) assisted deprotonation

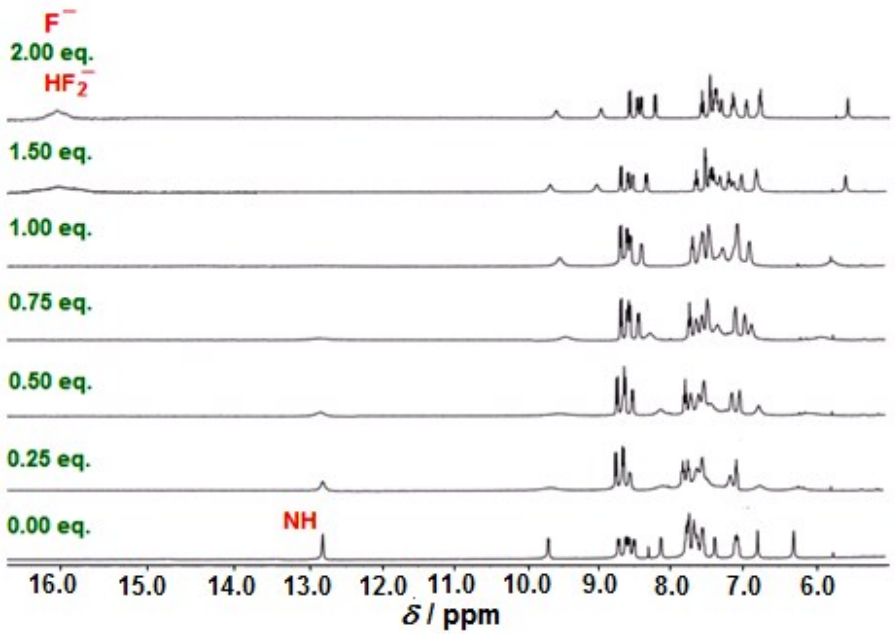


Fig. 8 ^{1}H-NMR titration of $\mathbf{1}^{+}$ in $(CD_3)_2SO$ in presence of TBA salt of F^- ion (0-2 equivalents).

of $\mathbf{1}^{+}$ or $\mathbf{2}^{+}$ has also been reflected in the upfield shifted CH proton singlets associated with the coordinated HL along with shifting of the bpy proton resonances. Similar ^{1}H-NMR spectral feature has also been obtained on interaction of OAc^- with $\mathbf{1}^{+}$ (Fig. S7†), although it fails to alter the ^{1}H-NMR of $\mathbf{2}^{+}$.

Furthermore, ^{19}F-NMR of TBAF was recorded which exhibits a characteristic peak at δ, −106.72 ppm in addition to a small peak for HF_2^- at δ, −144.94 ppm due to the effect of slight moisture content.[25] This signal for TBAF completely disappears on addition of one equivalent of $\mathbf{1}^{+}$ or $\mathbf{2}^{+}$, with a parallel effect of intensity enhancement of HF_2^- peak at −144.94 ppm (Fig. S8†), which possibly justifies the initial N-H···F hydrogen bonding interaction, followed by deprotonation and subsequent formation of HF_2^-.

In addition, ITC (Isothermal Titration Calorimetry) has also been performed to establish the receptor-anion interaction in terms of relevant thermodynamic parameters of the reaction involving the association constant (K), enthalpy ($\Delta H°$), entropy ($\Delta S°$) and stoichiometry (N) in a

single experiment.[25b,26] As a representative example, we have employed this experiment to ascertain the observed selectivity of $\mathbf{2}^+$ towards F^- ion *versus* the tested non-interacting anion such as I^-.

Fig. 9, refers to the integrated heat profile accompanying the titration of F^- and I^- ions with $\mathbf{2}^+$ at T = 298.15 K. The data fitted well with the sequential two binding sites model, showing complete saturation at the end of the titrations. The total heat (Q) produced or absorbed in the active cell volume (V_o) (relative to zero for the blank) at fractional saturation Θ after the i^{th} injection is given in eqn (1), where, C_t is the total concentration of $\mathbf{2}^+$ and ΔH^o is the molar heat of binding. The enthalpy change (ΔH_i) from the i^{th} injection with a volume dV_i is then derived by the eqn (2).[27]

$$Q = \Theta C_t \Delta H^o V_o \qquad (1)$$

$$\Delta H_i = Q_i + \frac{dV_i}{V_o}\left[\frac{Q(i) + Q(i-1)}{2}\right] - Q(i-1) \qquad (2)$$

As seen in Fig. 9, the interaction of F^- with $\mathbf{2}^+$ follows a typical sigmoidal binding pattern, leading to a saturation level. The recognition of F^- by $\mathbf{2}^+$ is marked by an exothermic event (ΔH_1^o= -56.7±0.4 kJ mol^{-1}) followed by an endothermic event (ΔH_2^o = 332.0 ± 2.5 kJ mol^{-1}), as reflected by the enthalpies of binding obtained by the analysis of the data according to sequential two binding sites model. The estimated binding constant values are, K_1 = (2.28±0.18)×10^4 M^{-1} and K_2 = (2.95±0.30)×10^5 M^{-1}. It is further observed that these two binding events are associated with an unfavourable entropic effect (ΔS_1^o = -0.11±0.02 kJ K^{-1} mol^{-1}) followed by a favourable contribution (ΔS_2^o = 1.22±0.08 kJ K^{-1} mol^{-1}). The first binding event with ΔG_1^o = -24.80±0.20 kJ mol^{-1} involves polar interactions due to hydrogen bond formation between the receptor and the anion, since such interactions are associated with exothermic heat effect[28]

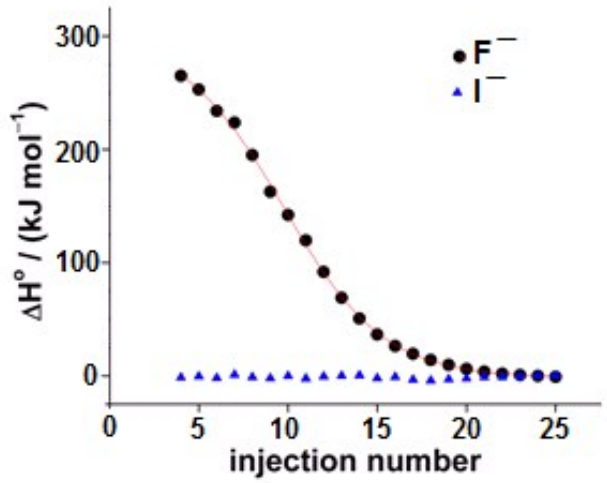


Fig. 9 Integrated isothermal titration calorimetric heat profile for the titration of F^- and I^- with $\mathbf{2}^+$ at T = 298.15 K.

followed by the second binding event with ΔG_2^o = -25.51±0.25 kJ mol^{-1} which has an endothermic enthalpy contribution involving the cleavage of the hydrogen bonded intermediate to **2** and forming HF_2^-, as stated below in eqn (3) and (4). On the other hand, the consecutive injections of I^- into the acetonitrile solution of $\mathbf{2}^+$ did not result in any appreciable heat change, suggesting the absence of recognition. The isothermal calorimetric measurements (Fig. 9) thus revealing the integrated heat profile accompanying the titration of $\mathbf{2}^+$ with F^- or I^-, are in agreement with the preceding experimental observations.

The experiments thus mentioned above collectively suggest a two step process between the receptor and anion, i.e. the association of receptor-anion, as also evident by the *in situ* mass experiment (Fig. S9†), leading to the eventual deprotonation. This two step process[2d,22a,29] can be expressed as:

$$[M(HL_n)]^+ + X^- \underset{}{\overset{K_a}{\rightleftharpoons}} [M(HL_n)]^+ \cdots X^-] \quad (3)$$

$$[M(HL_n)]^+ \cdots X^-] + X^- \underset{}{\overset{K_d}{\rightleftharpoons}} [M(L_n)] + HX_2^- \quad (4)$$

The minor change in the UV-vis spectra on addition of one equivalent of anion has restrained us to calculate log K_a (association constant) from the spectrophotometric titration. However, log K_d (dissociation constant) values have been calculated to be 6.57/5.91 (in case of $\mathbf{1}^+$ for F^-/OAc^-) and 6.17 (in case of $\mathbf{2}^+$ for F^-), as shown in Fig. S10†.

In general, the selective anion recognition features of $\mathbf{1}^+$ and $\mathbf{2}^+$ could tentatively be defined in terms of the basicity (pK_a(aq)) of the halogen acids and the oxy-anions: HF (3.45) > HCl(−7) > HBr (−9) > HI (−11) and HOAc (4.75) > H_3PO_4 (2.12) >H_2SO_4/HSCN (−2) > HNO_3 (−1.3).[30] However, the observed inertness of $\mathbf{2}^+$ towards OAc^- with even greater pK_a(aq) of HOAc than that of HF implies that the basicity of anion/receptor and the strength of hydrogen bonding interaction collectively control the proton transfer process from the receptor to the anion.[30*b*]

The stoichiometry of 1:2 between the receptor and anion as established in the preceding sections has also been ascertained by monitoring the change in reversible Os^{II}/Os^{III} oxidation(Ox1) process of $\mathbf{1}^+$ and $\mathbf{2}^+$ (Fig. 4) as a function of varying equivalents of aforesaid anions in CH_3CN (Fig. 10). The Ox1 potential of $\mathbf{1}^+$ or $\mathbf{2}^+$ at 0.32 V or 0.28 V in CH_3CN (Fig. 4) remains unchanged on addition of up to eight equivalents of Cl^-, Br^-, I^-, SCN^-, NO_3^-, HSO_4^- and $H_2PO_4^-$. However, an appreciable decrease in the oxidation potential has selectively been taken place on addition of two equivalents of F^-/OAc^- to $\mathbf{1}^+$ (-0.07 V) and F^- to $\mathbf{2}^+$ (-0.16 V). The lowering in potential on addition of anion is due to the increase in electron density on the metal centre by the anion mediated deprotonation of the coordinated HL, i.e the effect of the changeover of an weakly π-accepting HL in $\mathbf{1}^+$/$\mathbf{2}^+$ to the weakly π-donating L^- in **1**/**2**.

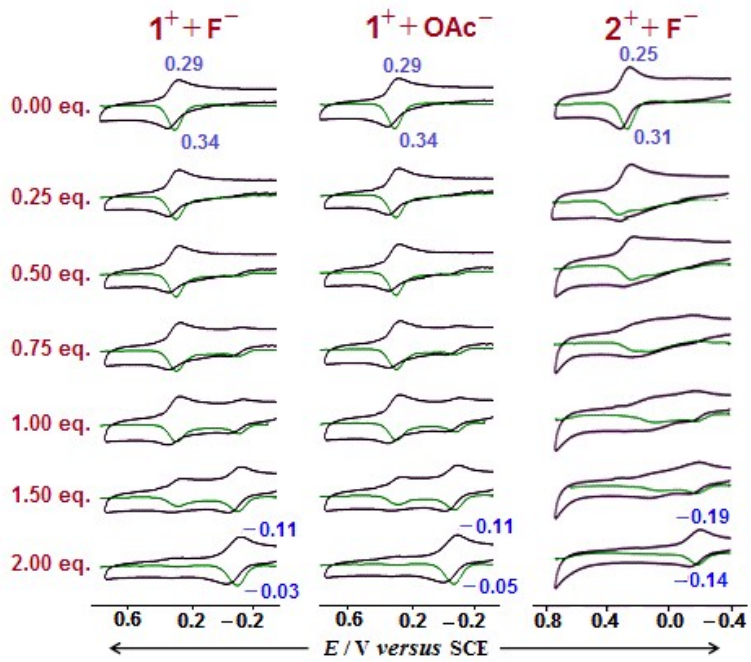


Fig. 10 Sequential changes in voltammograms (black) and differential pulse voltammograms (green) (reversible oxidation couple (Ox1 in Fig. 4) only) of $\mathbf{1}^+$ and $\mathbf{2}^+$ in CH_3CN ($5x10^{-5}$ mol dm^{-3}) upon gradual additions of anions.

The DFT (NBO) calculations have been performed to understand the mode of interaction between the receptors ($\mathbf{1}^+/\mathbf{2}^+$) and the anions ($X=F^-/OAc^-$). The lengthening of N(2)-H(2) distance (1.607 Å, 1.589 Å/1.719 Å) in optimised **A**/**A**$^/$/**B** (i.e. $\mathbf{1}^+/\mathbf{2}^+\cdots X^-$) as compared to that of 1.022 Å in optimised $\mathbf{1}^+/\mathbf{2}^+$ (Figs. S11, S12†), along with the shortening of H(2)-X^- distance by 0.984 Å, 0.992 Å/1.017 Å (Table 4) collectively suggest the intermediate hydrogen bonding interaction between the receptor and anion followed by breaking of N(2)-H(2) bond with a concomitant formation of H(2)-X bond. The N(2)-H(2)-X angles of 167.8^o, 163.3^o/165.2^o and D(donor)···A(acceptor) distances of 2.579 Å, 2.556 Å/2.715 Å in **A**/**A**$^/$/**B** (Table 4) also corroborate the hydrogen bond mediated deprotonation process.[4] The decrease in natural charge over N(2) and increase in natural charge over H(2) in the optimised structures of **A**/**A**$^/$/**B** with

Table 4 DFT calculated structural parameters and NBO charges

Complex	X^-	*d*(N2-H2) Å	*d*(H2···X) Å	*α*(N2-H2-X)°	q_N	q_H	q_X	q_{Os}
$\mathbf{1}^+$	-	1.022	-	-	-0.319	0.461	-	0.227
A	F^-	1.607	0.984	167.8	-0.357	0.549	-0.623	0.258
B	OAc^-	1.719	1.017	165.2	-0.383	0.522	-0.592	0.274
$\mathbf{2}^+$	-	1.022	-	-	-0.327	0.452	-	0.231
$\mathbf{A}^/$	F^-	1.589	0.992	163.3	-0.362	0.548	-0.624	0.262

respect to $\mathbf{1}^+/\mathbf{2}^+$ (Table 4) also endorse the above consideration.[4] The slight increment of the natural charge on Os in **A**/$\mathbf{A}^/$/**B** is a mere reflection of the change in the electronic environment around the metal centre in the presence of anions.

A close look at the DFT optimised structures of [$\mathbf{1}^+$...F] and [$\mathbf{1}^+$...OAc] (Fig. S12†) reveals the rotation of the pyrazole plane in $\mathbf{1}^+$ while interacting with the OAc^-. Such rotation of the dimethyl substituted pyrazole might have been restricted in $\mathbf{2}^+$ due to the steric reason which possibly can account for its exclusive selectivity towards the F^- over OAc^-.

Conclusions

In conclusion, osmium-coordinated pyrazolyl framework, $[(bpy)_2Os^{II}(HL_1)Cl]^+$ [**1**]ClO_4 or $[(bpy)_2Os^{II}(HL_2)Cl]^+$ [**2**]ClO_4 (HL_1 = pyrazole, HL_2 = 3,5-dimethylpyrazole) has been designed with the primary objective of exploring its feasibility to function as an efficient receptor for the selective anion recognition process. The structural analysis of [**1**]ClO_4 or [**2**]ClO_4 extends the additional features of intramolecular N-H···Cl and intermolecular N-H···O(ClO_4) hydrogen bonding interactions, revealing the fact of lesser accessibility of the NH proton of coordinated HL for the possible interaction with the incoming anions as has also been ascertained by its high pK_a value ($\mathbf{1}^+$: ~12.3, $\mathbf{2}^+$: >13.0). The impact of substituent in the framework of HL (H($\mathbf{1}^+$) *versus*

Me($\mathbf{2}^+$)) on the acidity of the NH protons has in turn made $\mathbf{2}^+$ exclusively selective for the F^- ion, while $\mathbf{1}^+$ recognises both F^- and OAc^-.

Experimental section

Materials

The metal precursor *cis*-$[Os^{II}(bpy)_2Cl_2]\cdot 2H_2O$[31] was prepared according to the literature procedure. Pyrazole (HL_1), 3,5-dimethylpyrazole (HL_2) and tetrabutylammonium salts of F^-, OH^-, Cl^-, Br^-, I^-, OAc^-, SCN^-, NO_3^-, HSO_4^-, $H_2PO_4^-$ were obtained from Sigma-Aldrich. All other chemicals and solvents were of reagent grade and used as received. For spectroscopic and electrochemical studies HPLC grade solvents were used.

Physical measurements

The electrical conductivities of the complexes in CH_3CN were checked by using an Autoranging conductivity meter (Toshcon Industries, India). ^{1}H-NMR and ^{19}F-NMR spectra were recorded using Bruker Avance III 400 and 500 MHz spectrometers. The elemental analyses were carried out on a Thermoquest (EA 1112) micro analyser. Electrospray mass spectra were recorded on a Bruker's Maxis Impact (282001.00081). Cyclic voltammetric and differential pulse voltammetric measurements were performed on a PAR model 273A electrochemistry system. $NEt_4^+ClO_4^-$ was used as the electrolyte and the solute concentration was ~10^{-3} mol dm^{-3}. A glassy carbon working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode (SCE) were used in a standard three-electrode configuration cell. A platinum wire-gauze working electrode was used for the constant potential coulometry experiment. All electrochemical experiments were carried out under dinitrogen atmosphere at 298 K. The half-wave potential E^0 was set equal to $0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic cyclic voltammetry peak potentials, respectively. Spectroelectrochemical studies were performed on a BAS SEC2000 spectrometer system. The supporting electrolyte was $NEt_4^+ClO_4^-$ and the

solute concentration was 10^{-5} mol dm^{-3}. UV-vis studies were performed on a Perkin-Elmer Lambda 1050 spectrophotometer. FT-IR spectra were taken on a Nicolet spectrophotometer with samples prepared as KBr pellets. Isothermal titration calorimetry (ITC) measurement was performed using NANO ITC, procured from TA instruments, New Castle, USA.

For spectrophotometric titrations, in each step 2 μL aliquot of the TBA salt of the respective anions ($5x10^{-3}$ mol dm^{-3}) in CH_3CN was added by a micro-syringe in 2 cm^3 CH_3CN solution of $\mathbf{1}^+$ or $\mathbf{2}^+$ ($5x10^{-5}$ mol dm^{-3}) using a quartz cuvette with 1 cm path length. Based on the spectrophotometric titrations, log K_d has been calculated using eqn (5)[32] where ΔA represents the

$$\Delta A = \frac{\Delta\varepsilon([M(HL_n)^+] + 1/K_d) + (\Delta\varepsilon^2([M(HL_n)^+] + [X^-] + 1/K_d)^2 - 4\Delta\varepsilon^2[(M(HL_n)^+][X^-])^{1/2}}{2} \quad (5)$$

change in initial absorbance upon each addition of the anions (X^-=F/OAc) in $\mathbf{1}^+$ or $\mathbf{2}^+$. $[M(HL_n)^+]$ and $[X^-]$ correspond to their respective concentrations during the spectrophotometric titrations. The disscociation constant (K_d) and the change in molar extinction coefficient ($\Delta\varepsilon$) at each concentration of F^-/OAc^- for $\mathbf{1}^+$ and F^- for $\mathbf{2}^+$ are evaluated by the nonlinear curve fitting procedure. For electrochemical titration, 25 μL aliquot of the TBA salt of the respective anions ($5x10^{-3}$ mol dm^{-3}) in acetonitrile was added by a micropipette in each step in 20 cm^3 acetonitrile solution of $\mathbf{1}^+$ or $\mathbf{2}^+$ ($5 x10^{-5}$ mol dm^{-3}). For isothermal titration calorimetric measurements, the solution of F^- or I^- prepared in acetonitrile was titrated into the sample cell in aliquots using a 250 μL stirrer-syringe rotating at a speed of 250 rpm. The calorimeter consists of a matched pair of sample and reference cells, each having a volume of 1.0 cm^3, placed in an adiabatic enclosure. The reference cell was filled with acetonitrile and closed with the cap provided with the calorimeter. The sample cell contained the compound $\mathbf{2}^+$ in acetonitrile. Each experiment consisted of 25 consecutive injections of 10 μL of 1 mmol dm^{-3} F^- /I^- solution into 0.01 mmol

dm^{-3} $\mathbf{2}^{+}$ taken in the cell for the duration of 6 s with 6 min interval between the consecutive injections. This arrangement provided sufficient time for the power signal to reach back the base line after each injection. Heats of dilution were obtained by titrating F^{-}/I^{-} or $\mathbf{2}^{+}$ with the solvent acetonitrile under the identical concentrations as used in the main experiment. The integrated heat profiles were corrected for the observed heats of dilutions.

Crystallography

Single crystals of [**1**]ClO_4 and [**2**]ClO_4 were grown by slow evaporation of their 1:1 dichloromethane-toluene solution. The X-ray crystal data were collected on RIGAKU SATURN-724+ CCD single crystal X-ray diffractometer. The data were collected by the standard omega scan technique and were scaled and reduced using the CrystalClear-SM Expert software. The structures were solved by direct method using SHELXS-97 and refined by full matrix least-squares with SHELXL2012, refining on F^2.[33] All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally $1.2U_{eq}$ of their parent atoms. Hydrogen atoms were included in the refinement process as per the riding model. CCDC-1430164 ([**1**]ClO_4) and 1430165 ([**2**]ClO_4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Computational details

Full geometry optimisations were carried out by using the density functional theory method at the (R)B3LYP level for $\mathbf{1}^{+}$, $\mathbf{2}^{+}$, **A**, $\mathbf{A}^{/}$, **B** and (U)B3LYP level for $\mathbf{1}^{2+}$, $\mathbf{1}^{3+}$, $\mathbf{2}^{2+}$, $\mathbf{2}^{3+}$, **1** and **2**.[34] All elements except osmium were assigned the 6-31G* basis set. The LANL2DZ basis set with

effective core potential was employed for the osmium atom.[35] The vibrational frequency calculations were performed to ensure that the optimised geometries represent the local minima and there are only positive eigen values. All calculations were performed with Gaussian09 program package.[36] Vertical electronic excitations based on (R)B3LYP/(U)B3LYP optimised geometries were computed for $\mathbf{1}^n$ (n = +2, +1) and $\mathbf{2}^n$ (n = +2, +1) using the time-dependent density functional theory (TD-DFT) formalism[37] in acetonitrile with the conductor-like polarisable continuum model (CPCM).[38] Natural bond orbital analysis was performed using the NBO 3.1 module of Gaussian 09 on optimised geometries. Chemissian *1.7*[39] was used to calculate the fractional contributions of various groups to each molecular orbital. All the calculated structures were visualised with ChemCraft.[40]

Preparation of complexes

Synthesis of $[Os^{II}(bpy)_2(HL_1)]ClO_4$, $[1]ClO_4$ and $[Os^{II}(bpy)_2(HL_2)]ClO_4$, $[2]ClO_4$. The precursor complex *cis*-$[Os^{II}(bpy)_2(Cl)_2]$ (100 mg, 0.17 mmol) and the ligand HL_1 (24 mg, 0.35 mmol) or HL_2 (33 mg, 0.35 mmol) were taken up in 30 cm^3 of 1:1 ethanol-water and the mixture was refluxed under dinitrogen atmosphere for 48 h. The initial light brown colour of the reaction mixture gradually changed to deep brown. The solvent was then removed under reduced pressure. The residue was moistened with a few drops of CH_3CN, followed by the addition of saturated aqueous $NaClO_4$ solution yielding a dark precipitate, which was filtered off, washed thoroughly with ice-cold water to remove the excess $NaClO_4$ and dried under vacuum. The crude product was purified on a neutral alumina column which led to the elution of the desired complex [**1**]ClO_4 by CH_3CN-MeOH (1:2) or [**2**]ClO_4 by CH_2Cl_2-CH_3CN (2:1). Evaporation of the solvent under reduced pressure yielded the pure complexes.

[1]ClO$_4$. Yield: 80 mg, 65%. Anal. calcd for $C_{23}H_{20}N_6O_4Cl_2Os$: C, 39.15; H, 2.86; N, 11.91; found: C, 39.23; H, 2.79; N, 11.82. Λ_M (Ω^{-1} cm^2 M^{-1}) in acetonitrile at 298 K: 115. ESI-MS(+) in CH_3CN, *m/z*: calcd for {**1**}$^+$: 607.096; found: 607.120. ^{1}H-NMR (500 MHz, DMSO-d$_6$): δ, (ppm, J(Hz)): 12.83 (s, 1H, NH), 9.69 (d, 1H, 5.1), 8.72 (d, 1H, 8.1), 8.62 (d, 1H, 8.1), 8.58 (d, 1H, 7.9), 8.51 (d, 1H, 8.0), 8.13 (d, 1H, 4.4), 7.77 (m, 3H), 7.65 (m, 3H), 7.55 (m, 2H), 7.38 (d, 1H, 5.2), 7.08 (m, 2H), 6.79 (s, 1H, CH), 6.29 (s, 1H, CH).

[2]ClO$_4$. Yield: 64 mg, 50%. Anal. calcd for $C_{25}H_{24}N_6O_4Cl_2Os$: C, 40.93; H, 3.30; N, 11.46; found: C, 40.72; H, 3.41; N, 11.29. Λ_M (Ω^{-1} cm^2 M^{-1}) in acetonitrile at 298 K: 110. ESI-MS(+) in CH_3CN, *m/z*: calcd for {**2**}$^+$: 635.125; found: 635.412. ^{1}H-NMR (400 MHz, DMSO-d$_6$): δ, (ppm, J(Hz)): 12.01 (s, 1H, NH), 9.81 (d, 1H, 5.6), 8.74 (d, 1H, 8.1), 8.57 (m, 2H), 8.41 (d, 1H, 8.2), 8.33 (d, 1H, 5.6), 7.71 (m, 5H), 7.55 (m, 1H), 7.48 (m, 1H), 7.34 (d, 1H, 5.5), 7.08 (m, 1H), 6.94 (m 1H), 5.84 (s, 1H, CH), 2.18 (s, 3H, CH_3), 1.29 (s, 3H, CH_3).

(*CAUTION*! Perchlorate salts are potentially explosive and should be handled with appropriate care).

Acknowledgements

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Table of Contents

Substituent directed selectivity in anion recognition by a new class of simple osmium-pyrazole derived receptor

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Remarkable impact of 3,5-dimethylpyrazole derived osmium framework with hydrogen bonded NH for the selective recognition of F^- has been ascertained.