# Supplementary Information

# Recognition of fractional non-innocent feature of osmium coordinated 2,2′-biimidazole or 2,2′-bis(4,5-dimethylimidazole) and their interactions with anions

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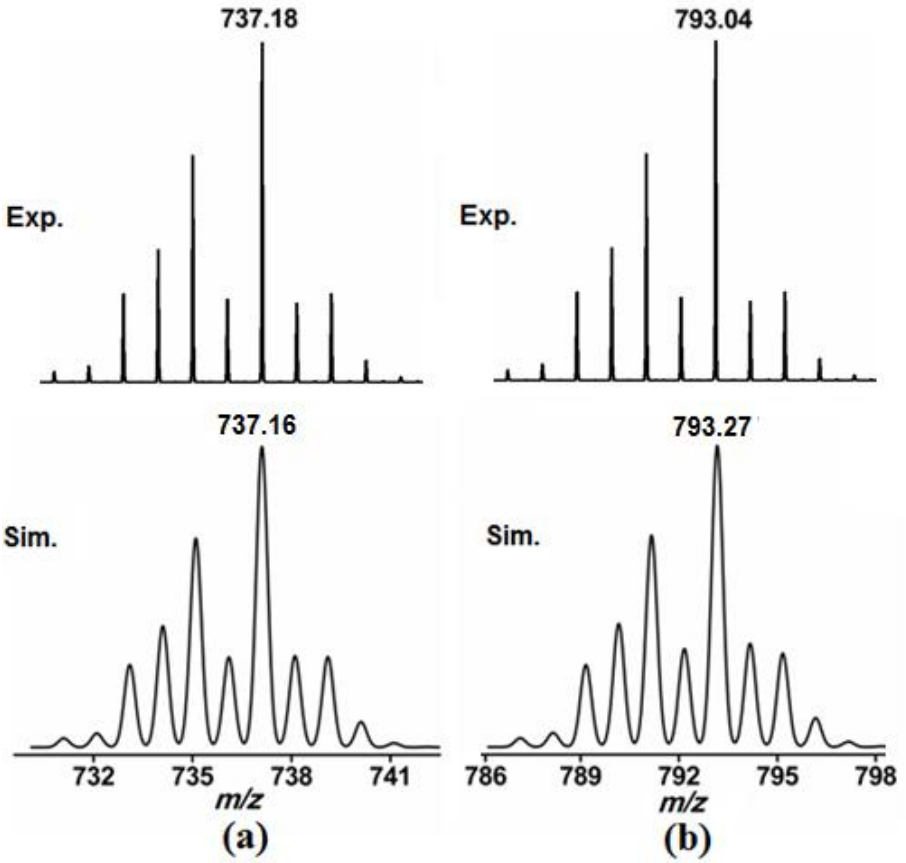



**Fig. S1** ESI-MS for (a) [**1**]$(ClO_4)_2$ and (b) [**2**]$(ClO_4)_2$ in $CH_3CN$.

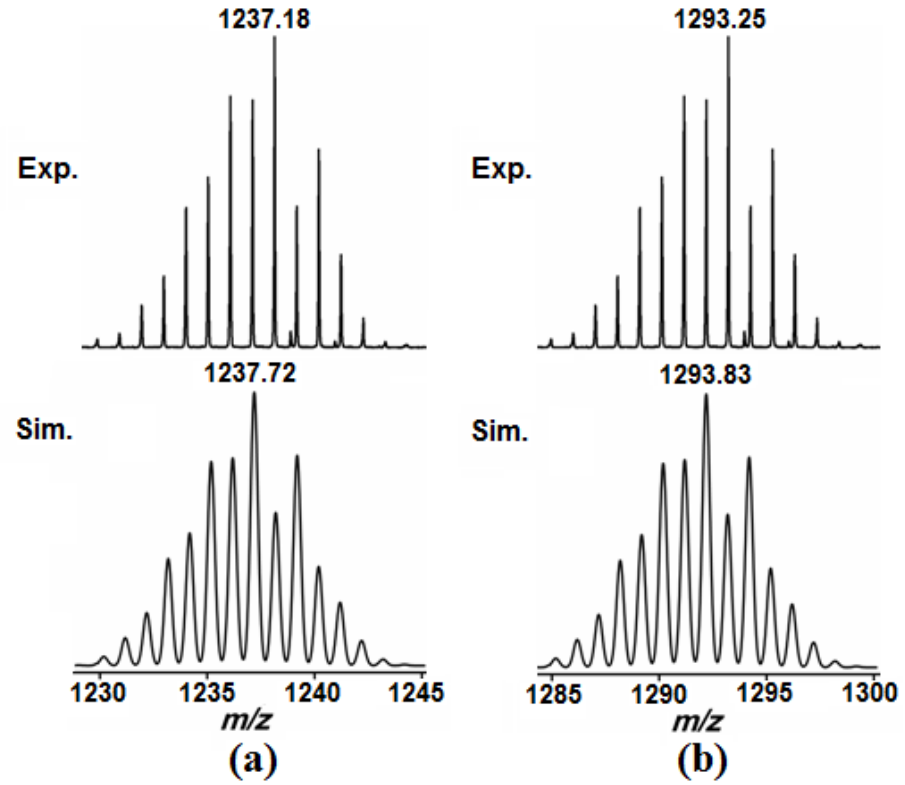



**Fig. S2** ESI-MS for (a) [**3**]$(ClO_4)_2$ and (b) [**4**]$(ClO_4)_2$ in $CH_3CN$.

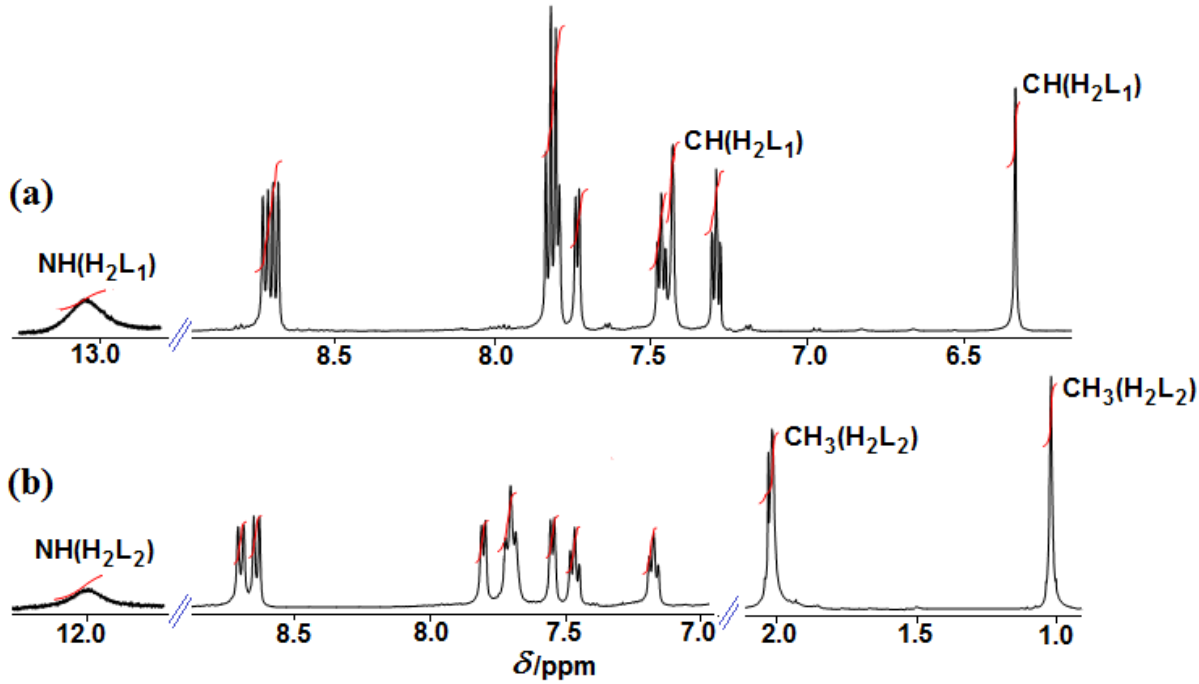



**Fig. S3** $^{1}$H-NMR spectra of (a) $\mathbf{1}^{2+}$ and (b) $\mathbf{2}^{2+}$ in DMSO-$d_6$.

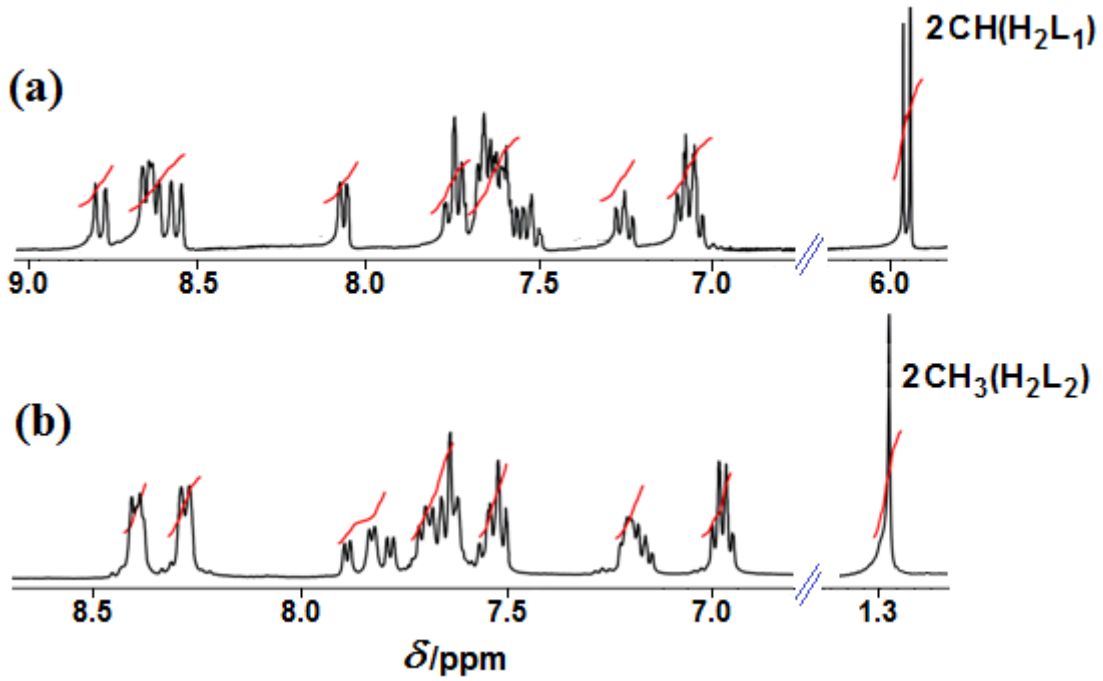



**Fig. S4** $^{1}$H-NMR spectra of (a) $\mathbf{3}^{2+}$ in DMSO-$d_6$ and (b) $\mathbf{4}^{2+}$ in $CD_3CN$.

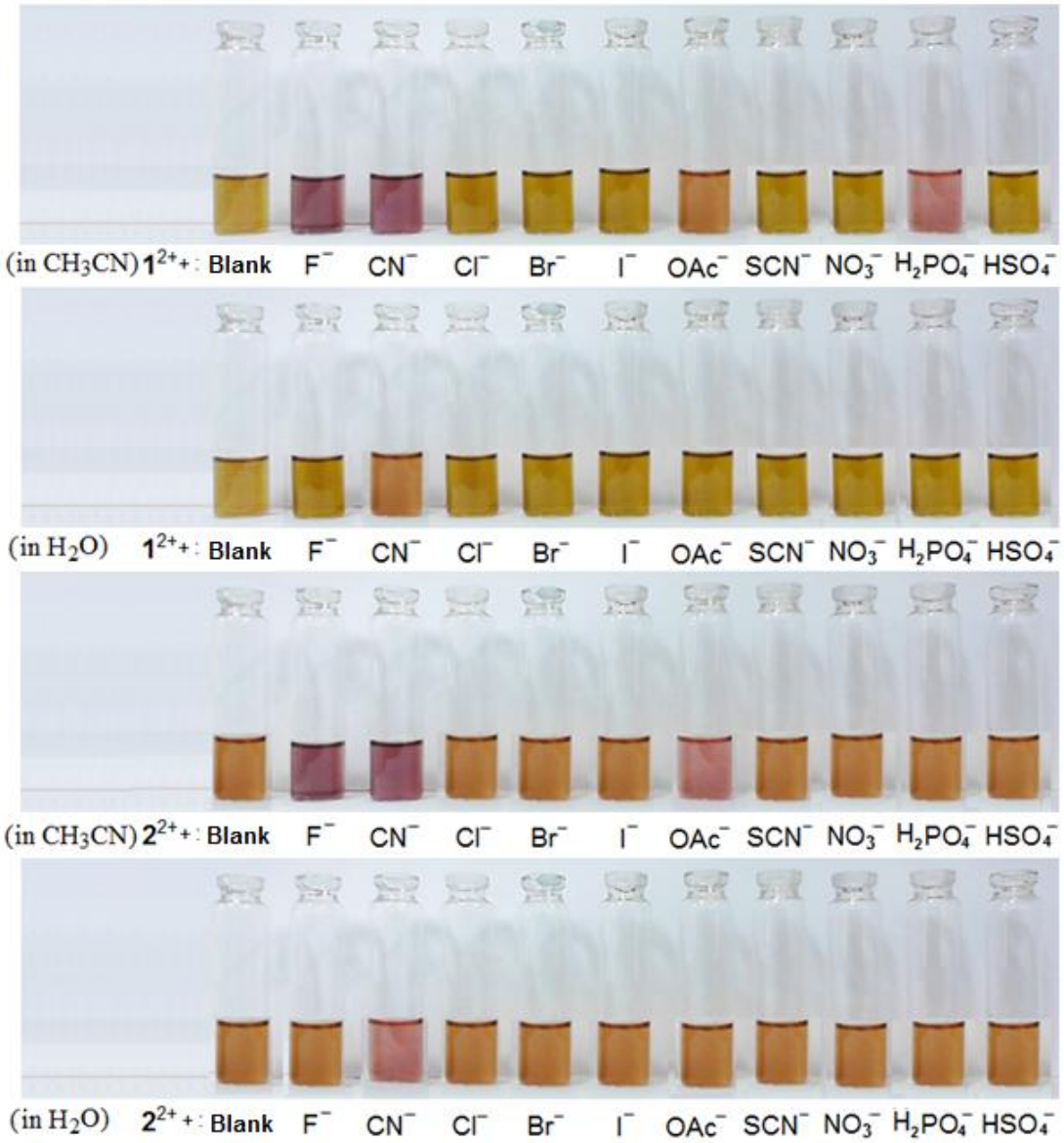



**Fig. S5** The visual change in colour of $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ ($5x10^{-5}$ mol $dm^{-3}$) in $CH_3CN$ and $H_2O$ on addition of eight equivalents of the TBA salts of $F^-$, $CN^-$, $Cl^-$, $Br^-$, $I^-$, $OAc^-$, $SCN^-$, $NO_3^-$, $H_2PO_4^-$ and $HSO_4^-$.

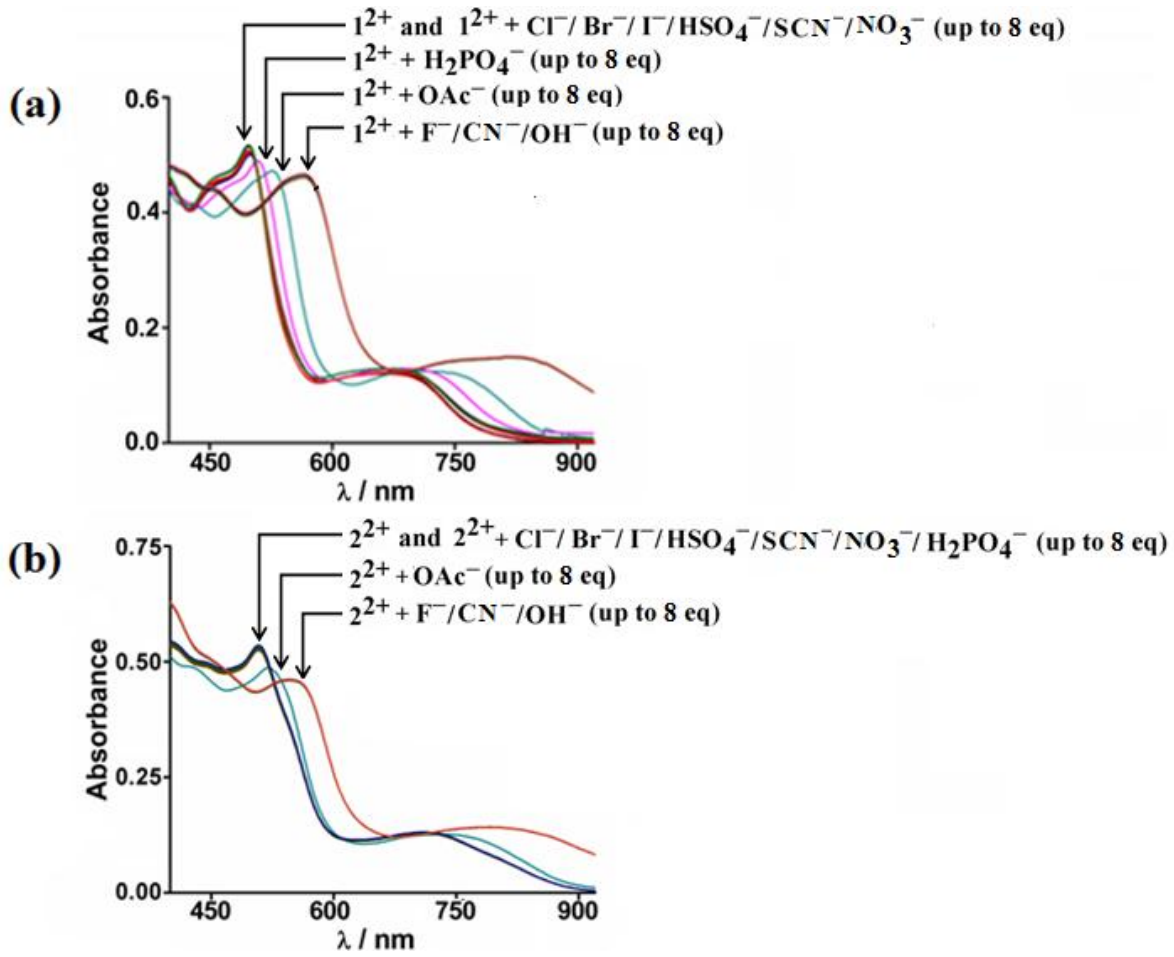



**Fig. S6** UV-vis. spectral changes of (a) $\mathbf{1}^{2+}$ and (b) $\mathbf{2}^{2+}$ (5 x $10^{-5}$ mol $dm^{-3}$) in $CH_3CN$ on addition of eight equivalents of the TBA salts of anions.

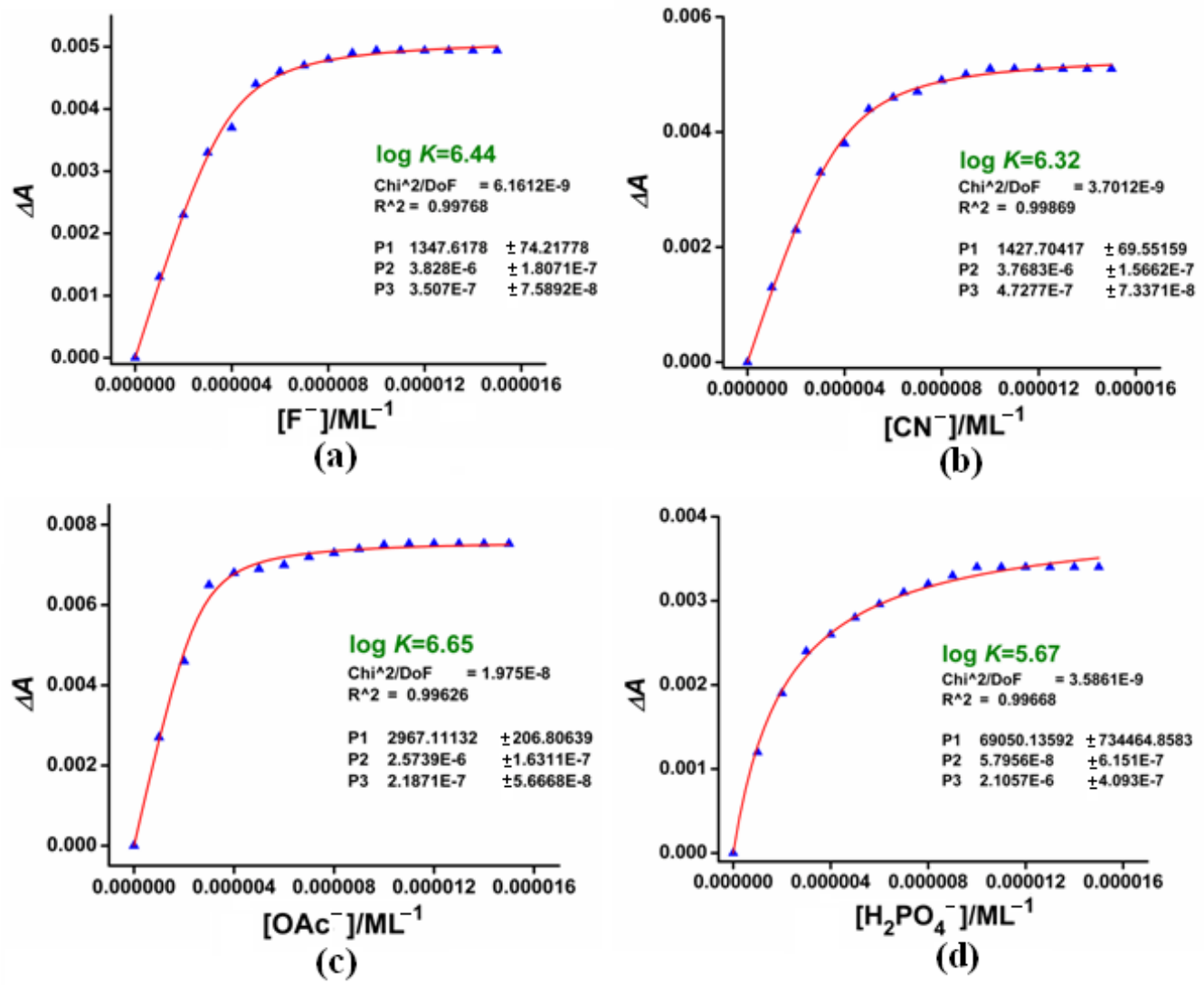



**Fig. S7** Plots of the changes in absorbance (*ΔA*) in $CH_3CN$ with respect to the initial absorbance of $\mathbf{1}^{2+}$ ($10^{-5}$ mol $dm^{-3}$) at 498 nm on each addition of (a) $F^-$ *versus* the concentration of $F^-$, (b) $CN^-$ *versus* the concentration of $CN^-$, (c) $OAc^-$ *versus* the concentration of $OAc^-$ and (d) $H_2PO_4^-$ *versus* the concentration of $H_2PO_4^-$.

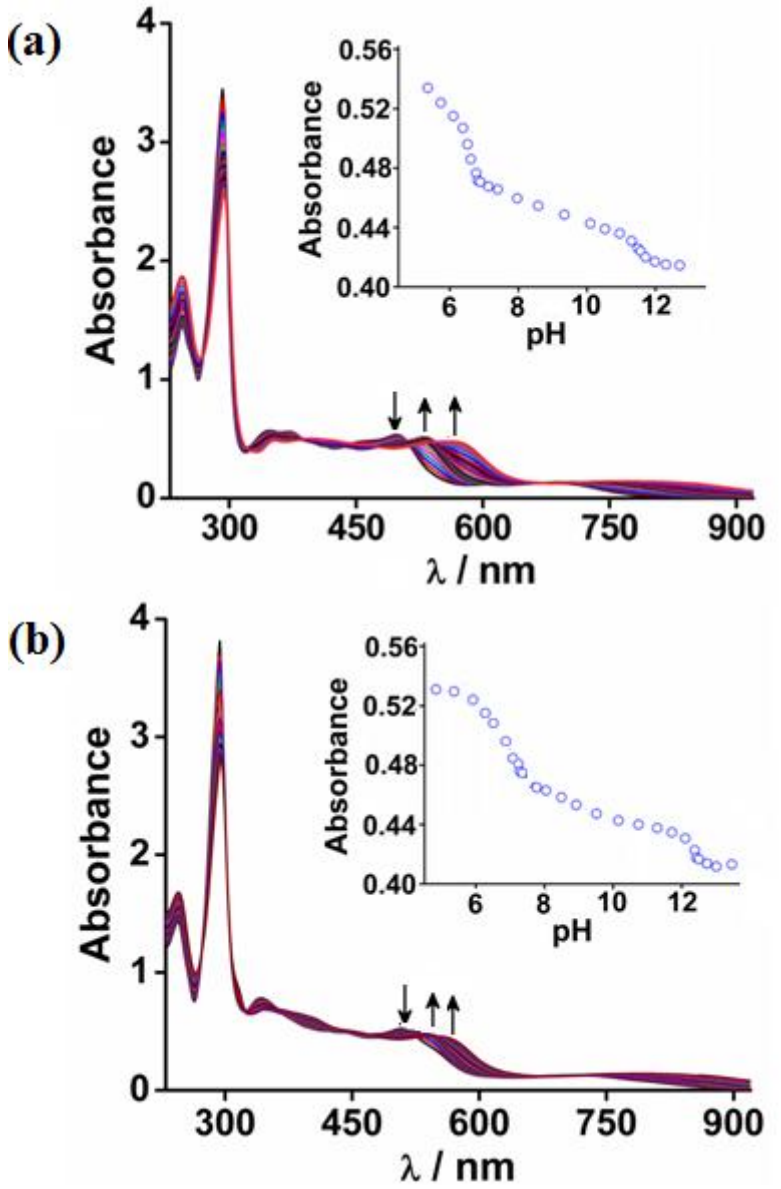



**Fig. S8** Electronic spectra of (a) $\mathbf{1}^{2+}$ and (b) $\mathbf{2}^{2+}$ as a function of pH in 1:1 $CH_3CN$-$H_2O$. Insets show the change in absorbance at (a) 530 nm and 565 nm for $\mathbf{1}^{2+}$ and (b) 545 nm and 560 nm for $\mathbf{2}^{2+}$ with the pH.

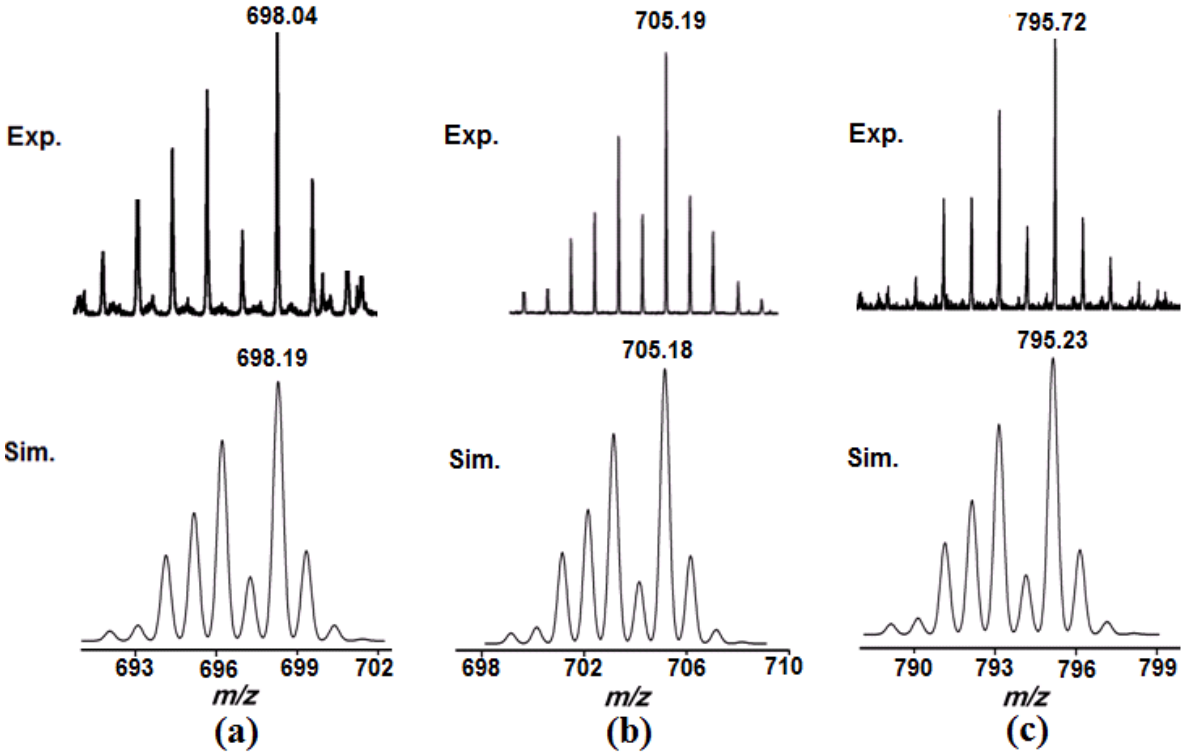



**Fig. S9** ESI-MS in $CH_3CN$ of (a) [$\mathbf{1}^{2+}$.$F^-$+$CH_3CN$], (b) [$\mathbf{1}^{2+}$.$CN^-$+$CH_3CN$] and (c) [$\mathbf{1}^{+}$.$OAc^-$] *in situ* generated by the addition of $F^-$, $CN^-$ and $OAc^-$, respectively, in the solution of $\mathbf{1}^{2+}$.

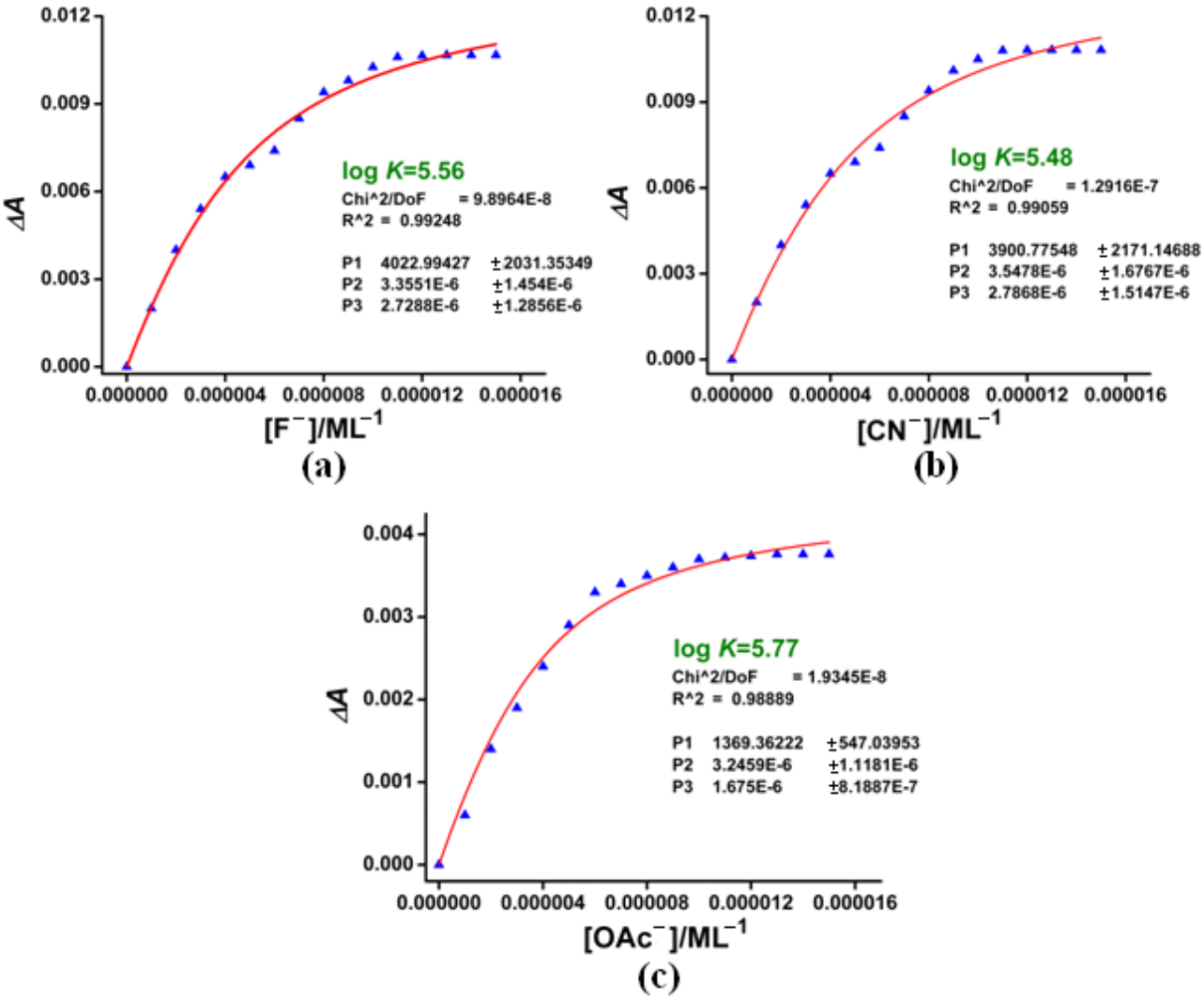



**Fig. S10** Plots of the changes in absorbance ($\Delta A$) in $CH_3CN$ with respect to the initial absorbance of $\mathbf{2}^{2+}$ ($10^{-5}$ mol $dm^{-3}$) at 508 nm on each addition of (a) $F^-$ *versus* the concentration of $F^-$, (b) $CN^-$ *versus* the concentration of $CN^-$ and (c) $OAc^-$ *versus* the concentration of $OAc^-$.

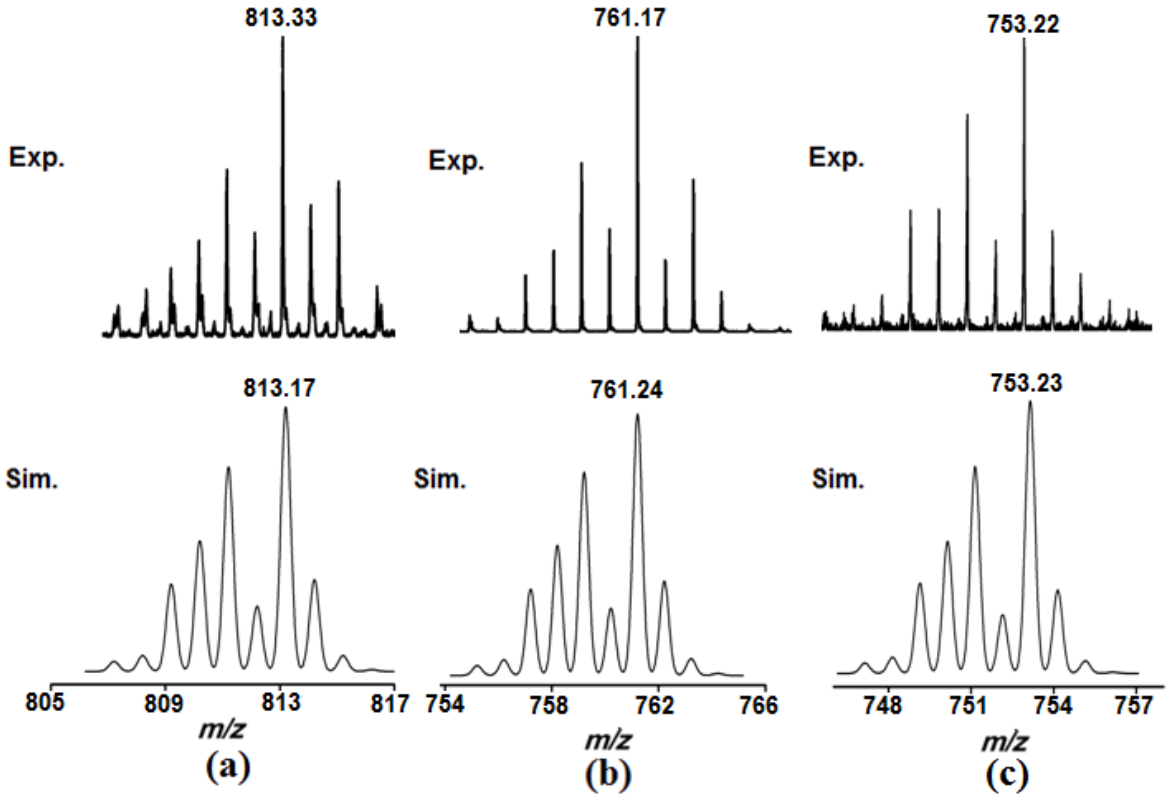



**Fig. S11** ESI-MS in $CH_3CN$ of (a) [$\mathbf{2}^{+}$.$F^{-}$+$H^{+}$], (b) [$\mathbf{2}^{2+}$.$CN^{-}$+$CH_3CN$] and (c) [$\mathbf{2}^{2+}$.$OAc^{-}$] *in situ* generated by the addition of $F^{-}$, $CN^{-}$ and $OAc^{-}$, respectively, in the solution of $\mathbf{2}^{2+}$.

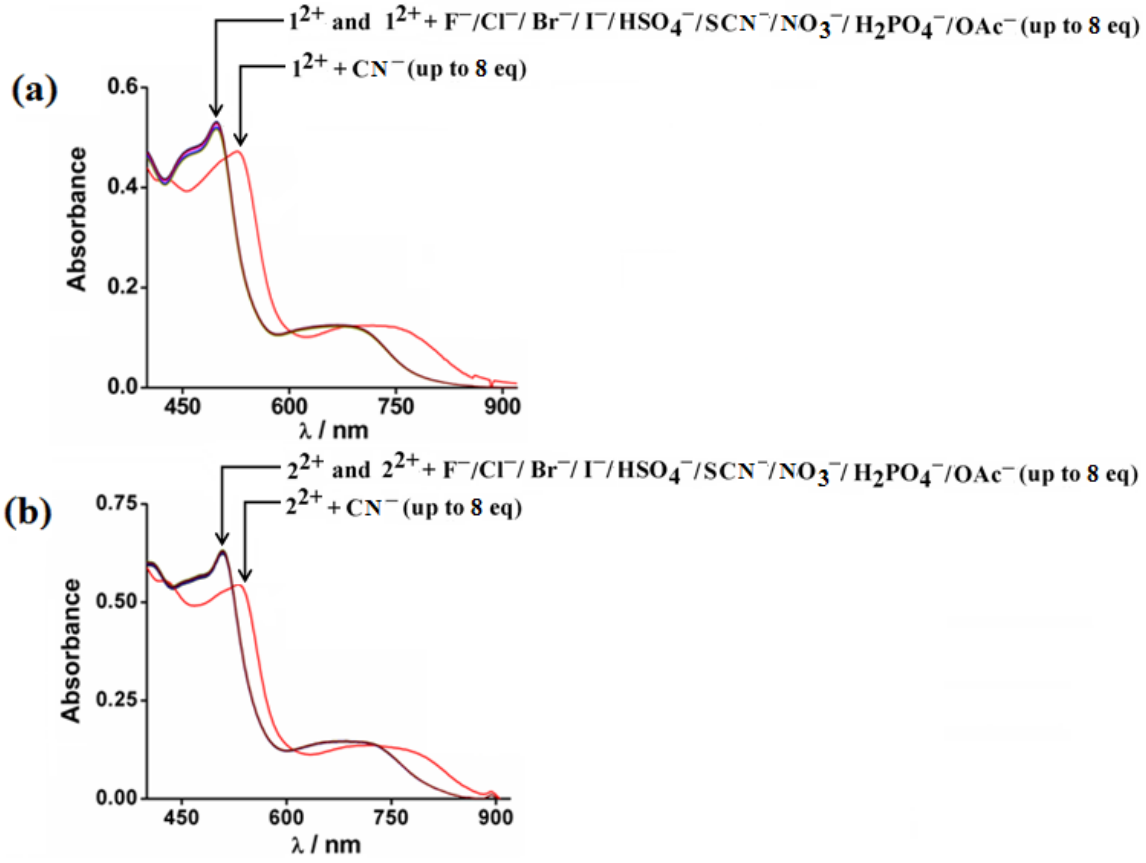



**Fig. S12** UV-vis. spectral changes of (a) $\mathbf{1}^{2+}$ and (b) $\mathbf{2}^{2+}$ (5 x $10^{-5}$ mol $dm^{-3}$) in $H_2O$ on addition of eight equivalents of the TBA salts of anions.

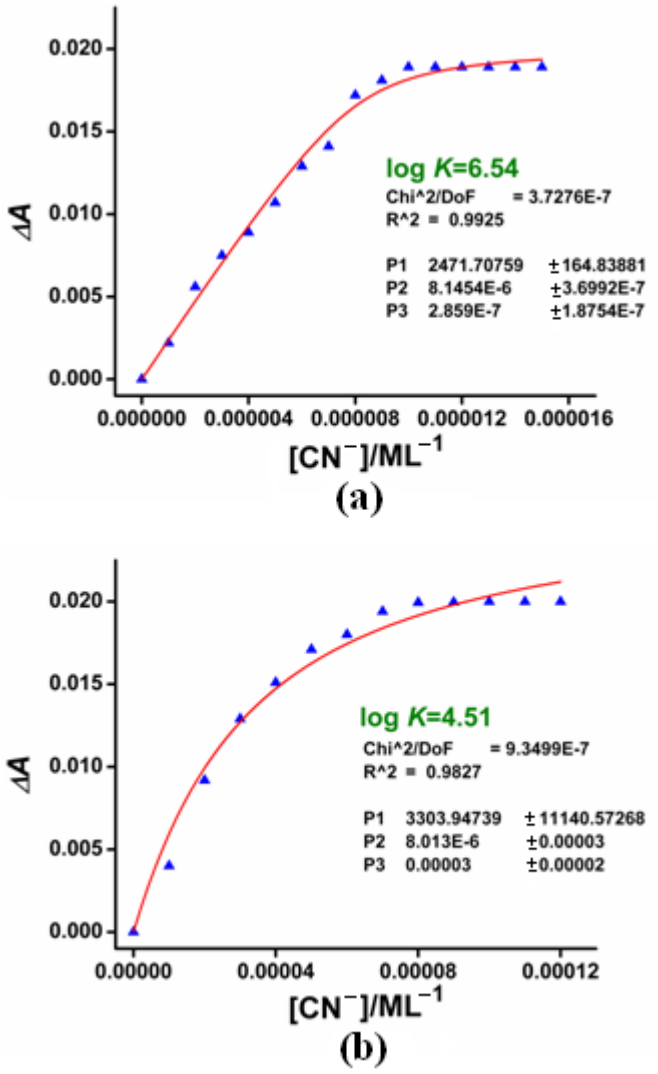



**Fig. S13** Plots of the changes in absorbance (*ΔA*) in aqueous medium with respect to the initial absorbance of (a) $\mathbf{1}^{2+}$ ($10^{-5}$ mol $dm^{-3}$) at 498 nm and (b) $\mathbf{2}^{2+}$ ($10^{-5}$ M) at 508 nm on each addition $CN^-$ *versus* the concentration of $CN^-$ .

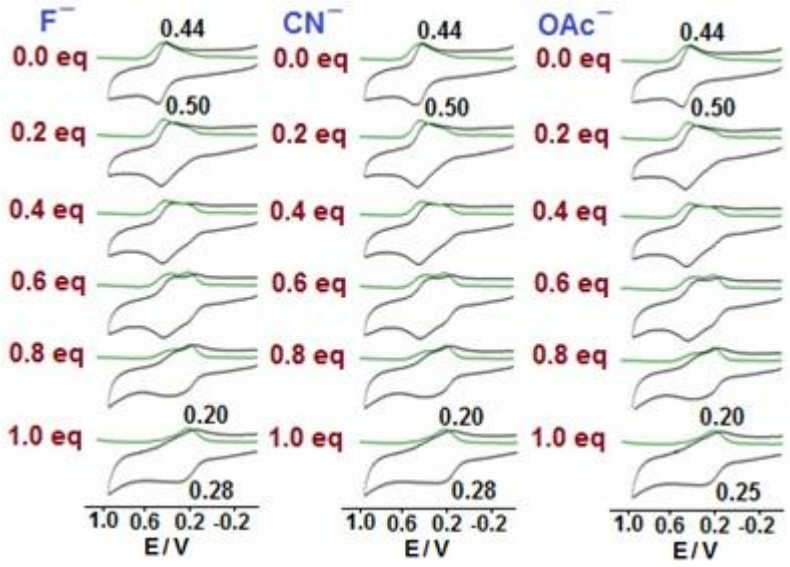



**Fig. S14** Sequential changes in voltammograms (black) and differential pulse voltammograms (green) (oxidation couple only) of $\mathbf{2}^{2+}$ in $CH_3CN$ ($10^{-3}$ mol $dm^{-3}$) upon gradual additions of anions.

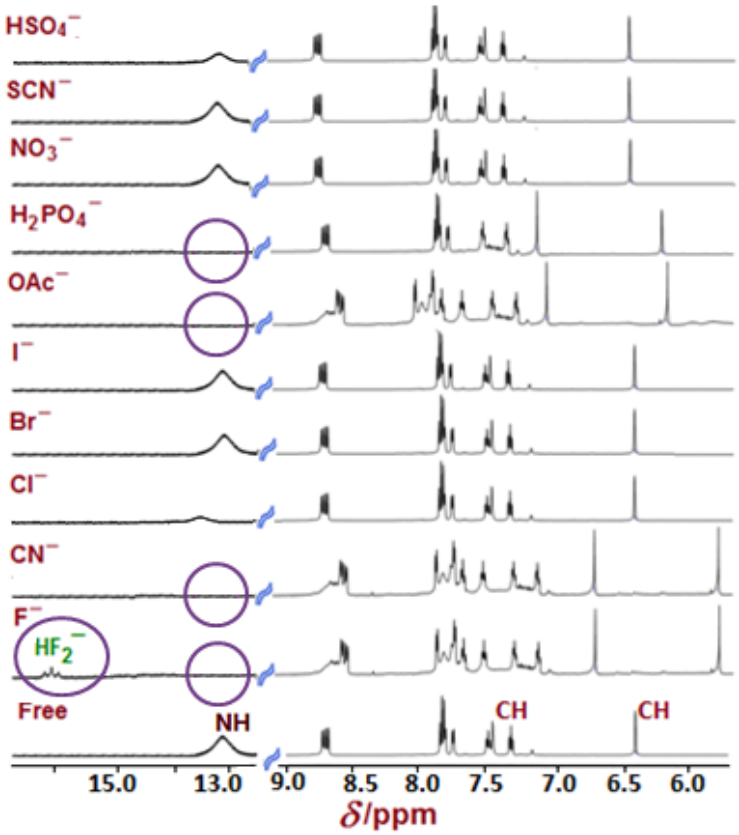



**Fig. S15** $^{1}$H-NMR spectra of free $\mathbf{1}^{2+}$ in DMSO-$d_6$ and in the presence of anions (up to 8 equivalents).

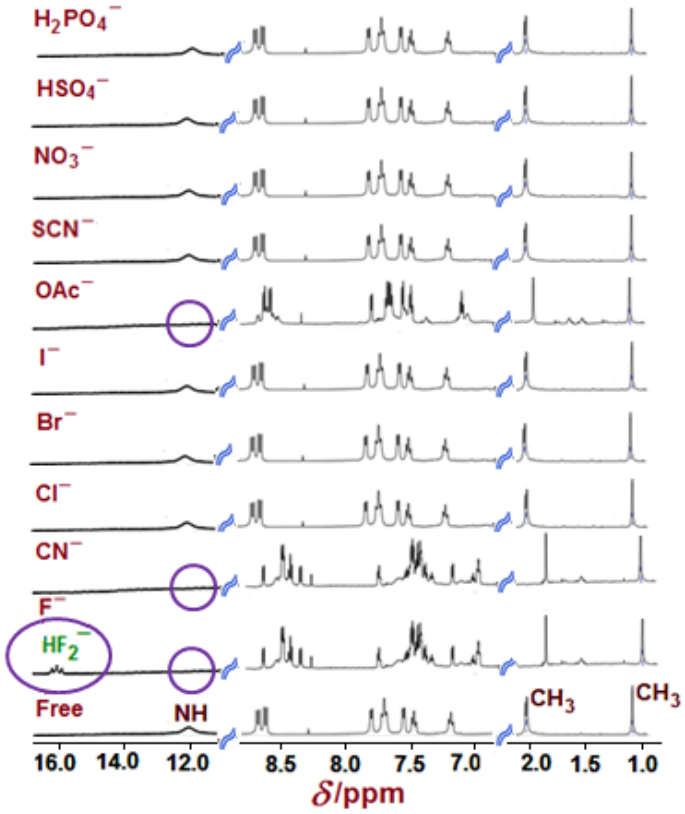



**Fig. S16** $^1$H-NMR titration of $\mathbf{2}^{2+}$ in DMSO-$d_6$ in the presence and absence of anions (up to 8 equivalents).

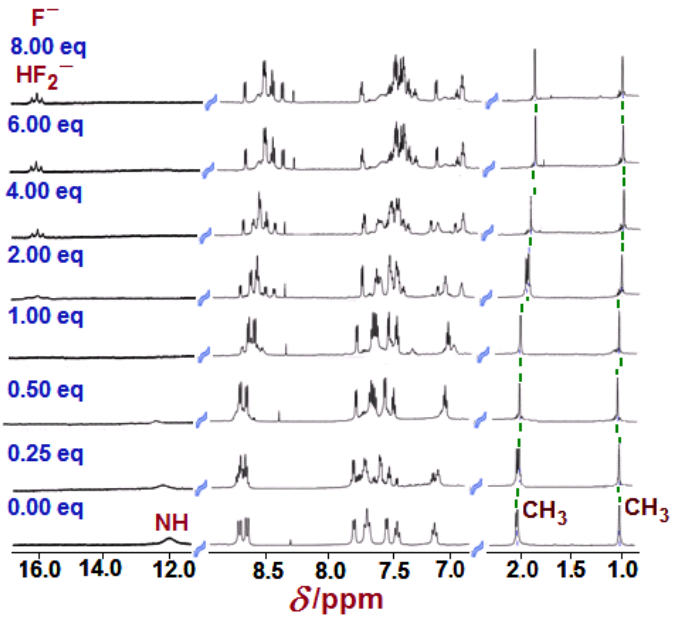



**Fig. S17** $^{1}$H-NMR titration of $\mathbf{2}^{2+}$ in DMSO-$d_6$ in presence of TBA salt of $F^-$ ion (0-8 equivalents).

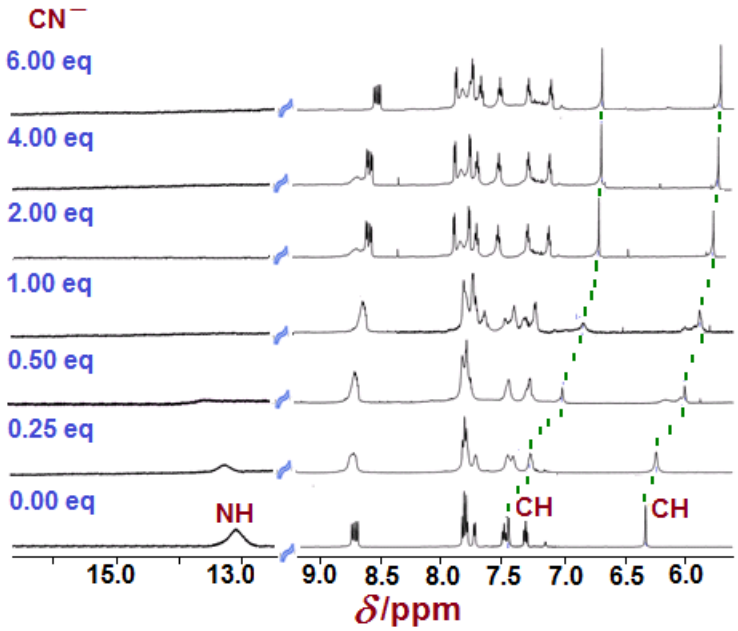



**Fig. S18** $^{1}$H-NMR titration of $\mathbf{1}^{2+}$ in DMSO-$d_6$ in presence of TBA salt of $CN^-$ ion (0-6 equivalents).

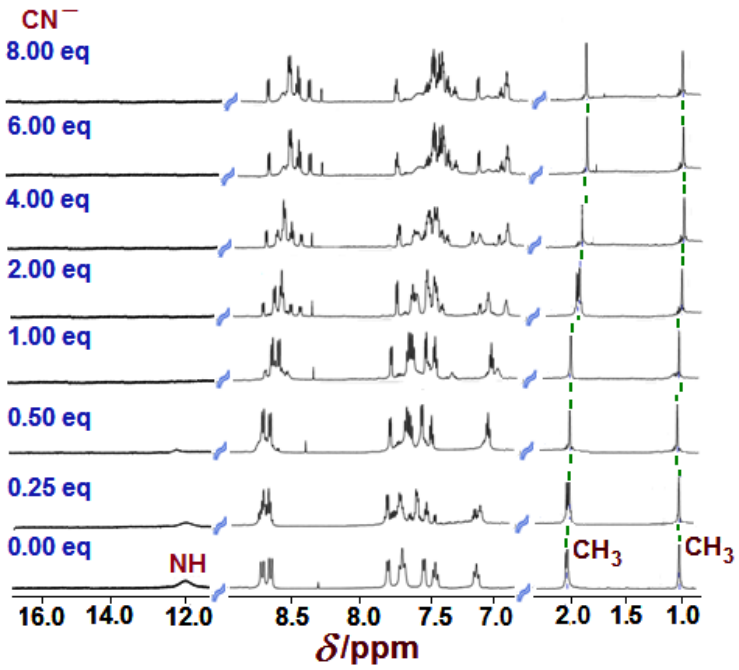



**Fig. S19** $^{1}$H-NMR titration of $\mathbf{2}^{2+}$ in DMSO-$d_6$ in presence of TBA salt of $CN^-$ ion (0-8 equivalents).

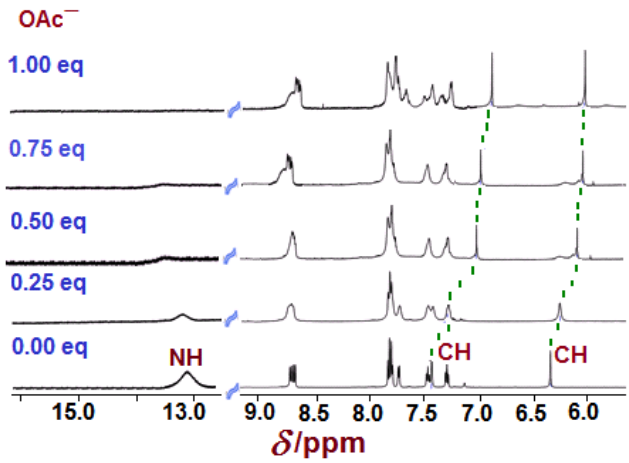



**Fig. S20** $^{1}$H-NMR titration of $\mathbf{1}^{2+}$ in DMSO-$d_6$ in presence of TBA salt of $OAc^-$ ion (0-1 equivalent).

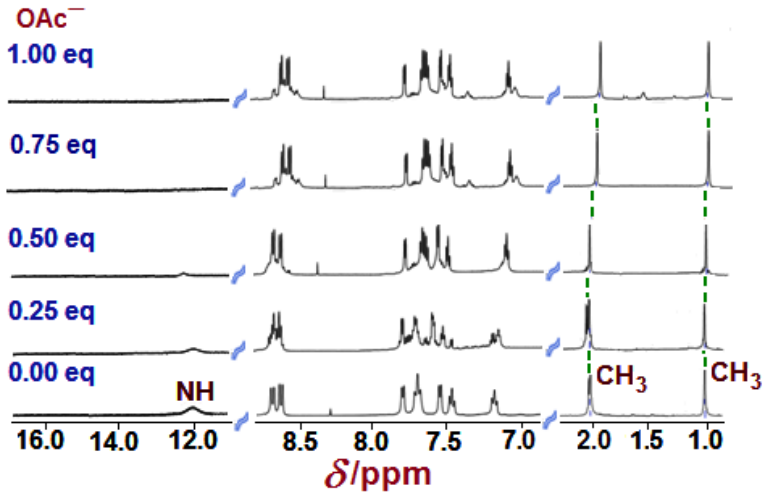



**Fig. S21** $^{1}$H-NMR titration of $\mathbf{2}^{2+}$ in DMSO-$d_6$ in presence of TBA salt of $OAc^-$ ion (0-1 equivalent).

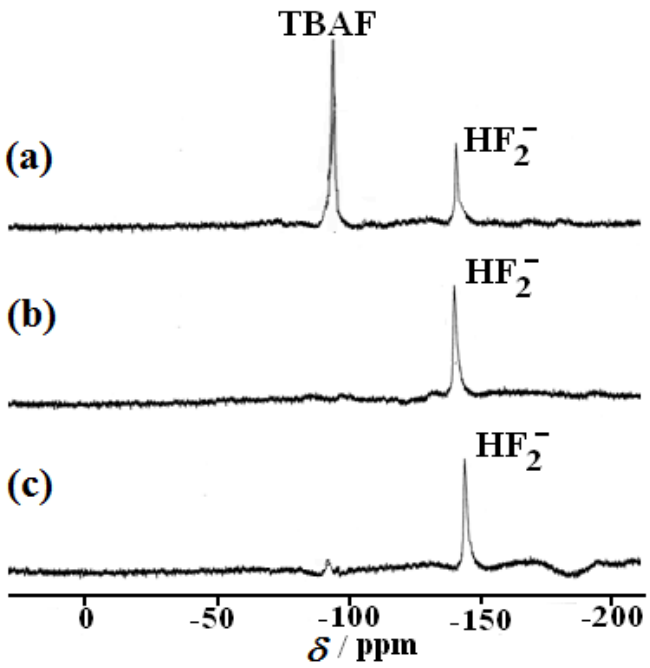



**Fig. S22** $^{19}$F-NMR spectra in DMSO-$d_6$ of (a) TBAF, (b) TBAF in presence of 0.4 equivalent of $\mathbf{1}^{2+}$ and (c) TBAF in presence of 0.4 equivalent of $\mathbf{2}^{2+}$. Trifluoro-toluene is used as an internal standard ($\delta$ = –62.23) at 298 K.

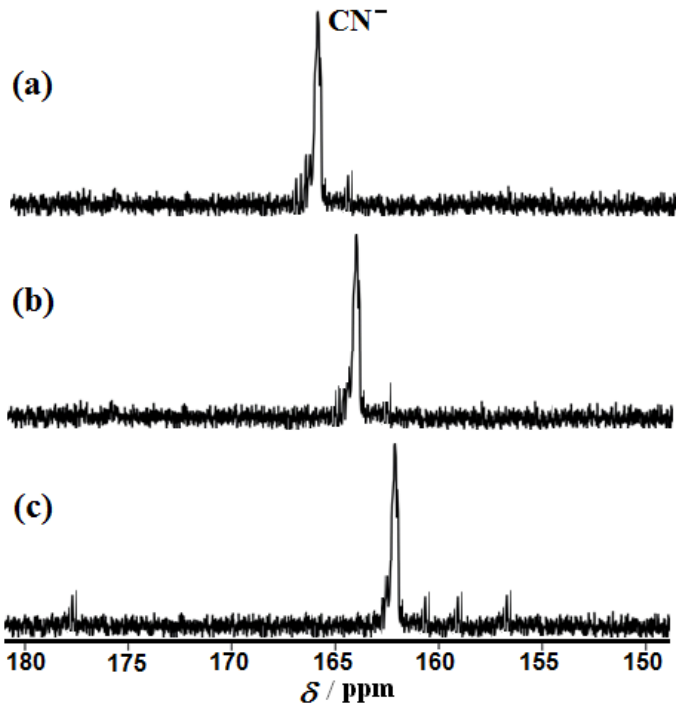



**Fig. S23** $^{13}$C-NMR spectra in DMSO-$d_6$ of (a) TBACN, (b) TBACN in presence of 1 equivalent of $\mathbf{1}^{2+}$ and (c) TBACN in presence of 1 equivalent of $\mathbf{2}^{2+}$.

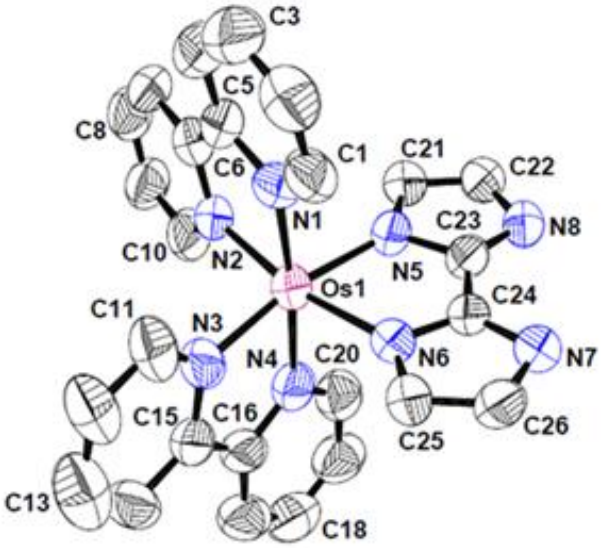
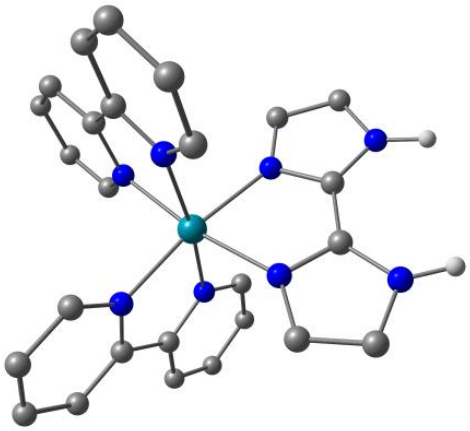
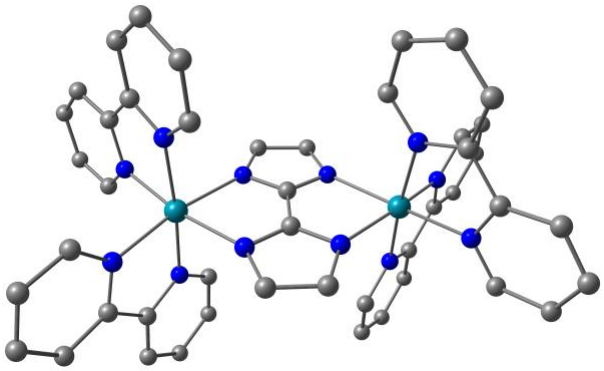


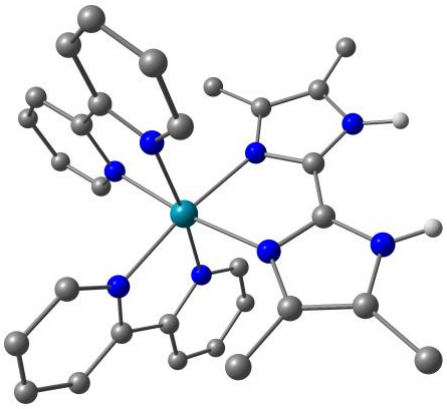

**Fig. S24** ORTEP diagram of **1**. Hydrogens are omitted for clarity. Ellipsoids are drawn at 30% probability level.



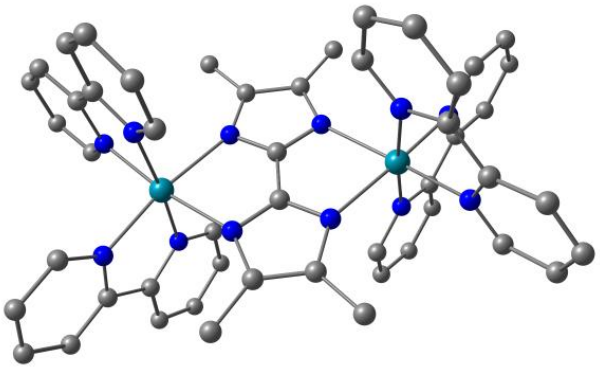
$\mathbf{1}^{2+}$



$\mathbf{3}^{2+}$



$\mathbf{2}^{2+}$



$\mathbf{4}^{2+}$

**Fig. S25** DFT optimised structures of $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$, $\mathbf{3}^{2+}$ and $\mathbf{4}^{2+}$.

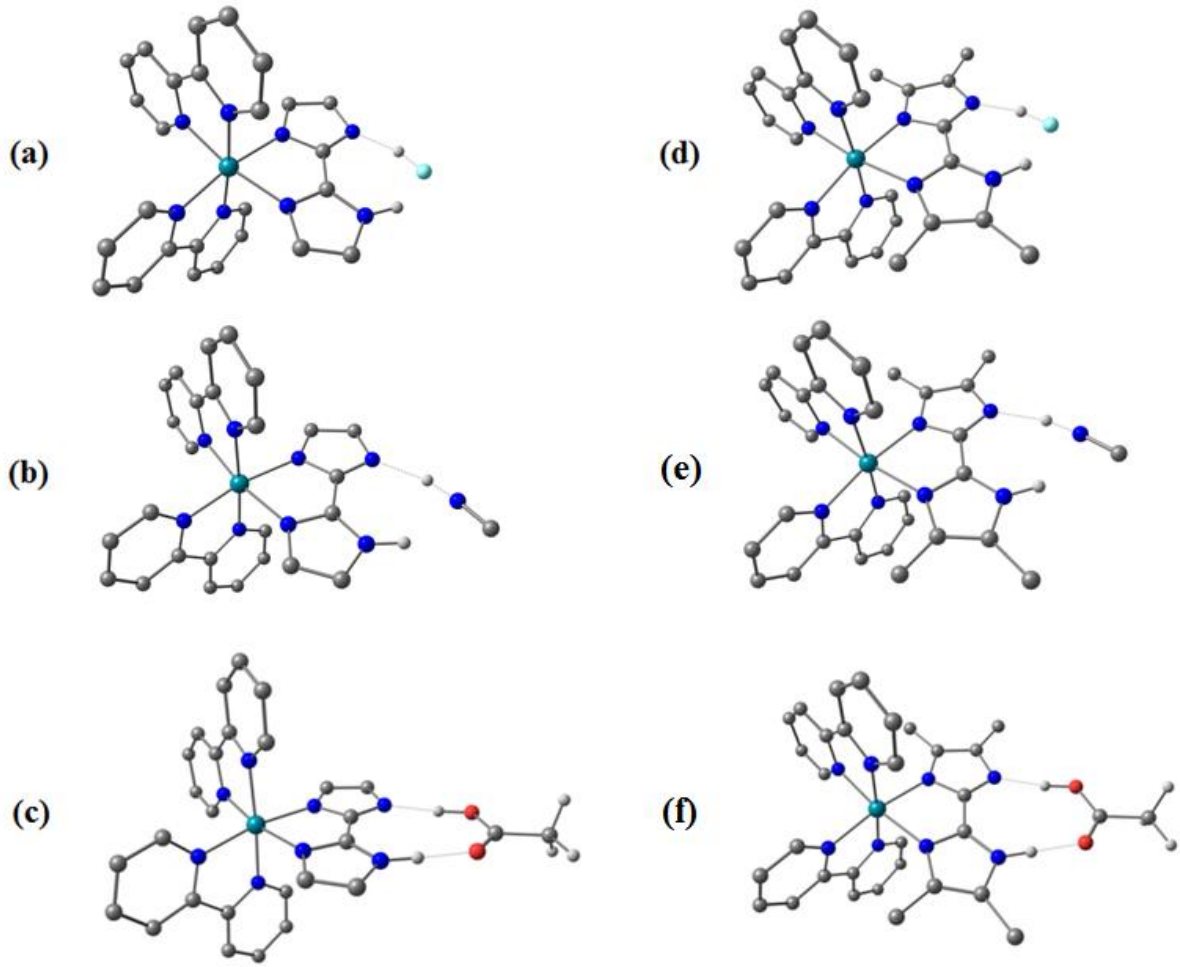



**Fig. S26** DFT optimised structures of (a) [$\mathbf{1}^{2+}$. $F^-$], (b) [$\mathbf{1}^{2+}$ . $CN^-$], (c) [$\mathbf{1}^{2+}$ . $OAc^-$], (d) [$\mathbf{2}^{2+}$. $F^-$], (e) [$\mathbf{2}^{2+}$.$CN^-$] and (f) [$\mathbf{2}^{2+}$.$OAc^-$].

**Table S1** Experimental (X-ray) and DFT calculated selected bond angles (°) for [**1**]$(ClO_4)_2$ and [**3**]$(ClO_4)_2$

| [**1**]$(ClO_4)_2$ | | | [**3**]$(ClO_4)_2$ | | |
|---|---|---|---|---|---|
| Bond angles (°) | X-ray | DFT | Bond angles (°) | X-ray | DFT |
| N1-Os1-N2 | 77.6(4) | 77.60 | N1-Os1-N2 | 78.9(3) | 77.98 |
| N1-Os1-N3 | 96.7(4) | 97.46 | N1-Os1-N3 | 94.9(3) | 98.46 |
| N1-Os1-N4 | 175.0(3) | 172.99 | N1-Os1-N4 | 173.9(3) | 174.89 |
| N1-Os1-N5 | 89.0(4) | 88.51 | N1-Os1-N5 | 95.8(3) | 95.31 |
| N1-Os1-N6 | 96.5(3) | 97.31 | N1-Os1-N6# | 89.8(3) | 88.92 |
| N2-Os1-N3 | 89.4(5) | 91.01 | N2-Os1-N3 | 98.7(3) | 94.36 |
| N2-Os1-N4 | 99.2(4) | 97.39 | N2-Os1-N4 | 100.4(3) | 98.50 |
| N2-Os1-N6 | 167.9(4) | 171.54 | N2-Os1-N6# | 90.1(3) | 93.52 |
| N2-Os1-N5 | 93.5(5) | 96.78 | N2-Os1-N5 | 170.2(3) | 170.67 |
| N3-Os1-N4 | 79.4(4) | 77.58 | N3-Os1-N4 | 79.2(3) | 77.99 |
| N3-Os1-N6 | 101.9(4) | 96.37 | N3-Os1-N6# | 170.7(3) | 170.14 |
| N3-Os1-N5 | 174.1(3) | 171.05 | N3-Os1-N5 | 89.9(3) | 93.03 |
| N4-Os1-N6 | 87.4(4) | 88.22 | N4-Os1-N6# | 96.3(3) | 95.02 |
| N4-Os1-N5 | 95.0(4) | 97.00 | N4-Os1-N5 | 85.7(3) | 88.58 |
| N5-Os1-N6 | 75.7(4) | 76.19 | N5-Os1-N6# | 81.6(2) | 79.74 |

**Table S2** Hydrogen bonding parameters (intermolecular) of [**1**]$(ClO_4)_2$ in (Å) and (º)

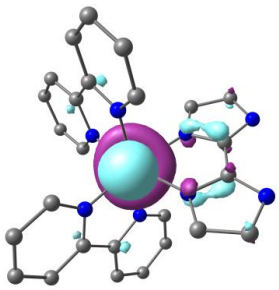
| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| N(7)-H(7)...O(7)#1 | 0.860 | 2.129 | 2.892 | 147.60 |
| N(8)-H(8)...O(6)#1 | 0.860 | 2.085 | 2.913 | 161.12 |

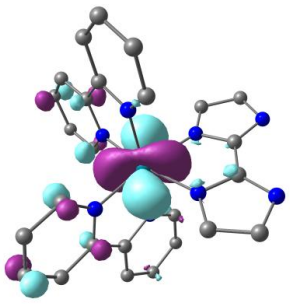
Symmetry transformations used to generate equivalent atoms:

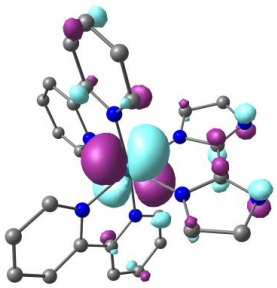
#1 x+1, y, z

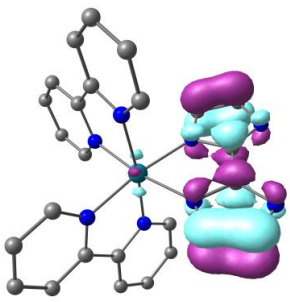
**Table S3** Selected molecular orbitals along with their energies and compositions of $\mathbf{1}^{2+}$ in *S*=0 state

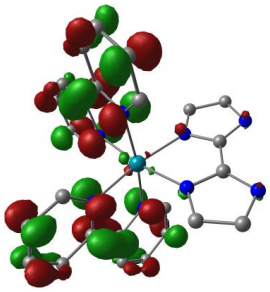
| MO | Energy(eV) | Composition | | |
|---|---|---|---|---|
| | | Os | $H_2L_1$ | bpy |
| HOMO–5 | –12.350 | 0.00 | 0.02 | 0.97 |
| HOMO–4 | –12.263 | 0.01 | 0.01 | 0.98 |
| HOMO–3 | –12.028 | 0.05 | 0.90 | 0.05 |
| HOMO–2 | –10.839 | 0.69 | 0.11 | 0.20 |
| HOMO–1 | –10.804 | 0.68 | 0.09 | 0.23 |
| HOMO | –10.639 | 0.74 | 0.10 | 0.16 |
| LUMO | –7.466 | 0.04 | 0.17 | 0.79 |
| LUMO+1 | –7.258 | 0.10 | 0.03 | 0.88 |
| LUMO+2 | –6.974 | 0.08 | 0.78 | 0.14 |
| LUMO+3 | –6.505 | 0.03 | 0.03 | 0.94 |
| LUMO+4 | –6.313 | 0.04 | 0.01 | 0.95 |
| LUMO+5 | –6.223 | 0.07 | 0.02 | 0.90 |

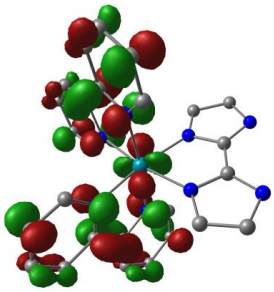

HOMO

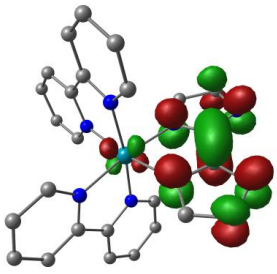

HOMO–1


HOMO–2


HOMO–3


LUMO


LUMO+1


LUMO+2

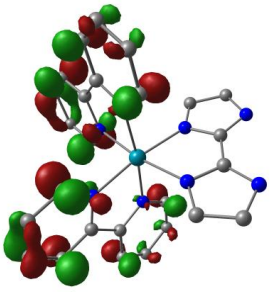

LUMO+3

**Table S4** Selected molecular orbitals along with their energies and compositions of $\mathbf{1}^{3+}$ in *S*=1/2 state

| MO | Energy(eV) | Composition | | |
|---|---|---|---|---|
| | | Os | $H_2L_1$ | bpy |
| | | α-spin | | |
| HOMO–5 | –15.968 | 0.59 | 0.09 | 0.32 |
| HOMO–4 | –15.392 | 0.30 | 0.05 | 0.64 |
| HOMO–3 | –15.371 | 0.17 | 0.03 | 0.79 |
| HOMO–2 | –15.232 | 0.51 | 0.08 | 0.41 |
| HOMO–1 | –15.227 | 0.55 | 0.07 | 0.38 |
| SOMO | –14.861 | 0.10 | 0.88 | 0.02 |
| LUMO | –10.703 | 0.04 | 0.04 | 0.93 |
| LUMO+1 | –10.624 | 0.07 | 0.01 | 0.92 |
| LUMO+2 | –10.326 | 0.05 | 0.90 | 0.04 |
| LUMO+3 | –9.675 | 0.03 | 0.02 | 0.95 |
| LUMO+4 | –9.539 | 0.02 | 0.01 | 0.97 |
| LUMO+5 | –9.461 | 0.01 | 0.01 | 0.99 |
| | | β-spin | | |
| HOMO–5 | –16.609 | 0.00 | 0.96 | 0.04 |
| HOMO–4 | –15.374 | 0.01 | 0.01 | 0.98 |
| HOMO–3 | –15.347 | 0.05 | 0.01 | 0.94 |
| HOMO–2 | –15.074 | 0.42 | 0.43 | 0.16 |
| HOMO–1 | –14.979 | 0.69 | 0.11 | 0.20 |
| HOMO | –14.803 | 0.38 | 0.48 | 0.13 |
| LUMO | –12.712 | 0.77 | 0.08 | 0.14 |
| LUMO+1 | –10.688 | 0.04 | 0.04 | 0.92 |
| LUMO+2 | –10.597 | 0.08 | 0.01 | 0.91 |
| LUMO+3 | –10.289 | 0.06 | 0.90 | 0.04 |
| LUMO+4 | –9.665 | 0.03 | 0.02 | 0.95 |
| LUMO+5 | –9.494 | 0.04 | 0.01 | 0.96 |

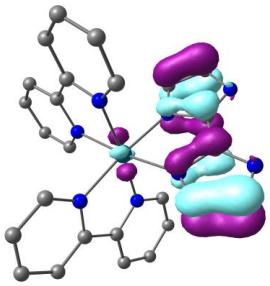
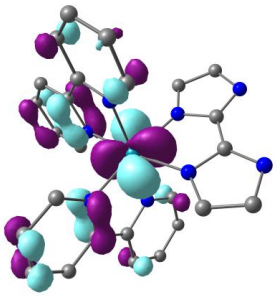
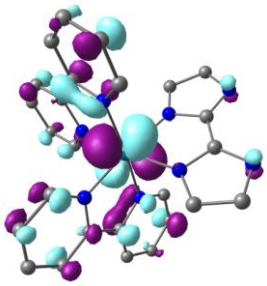
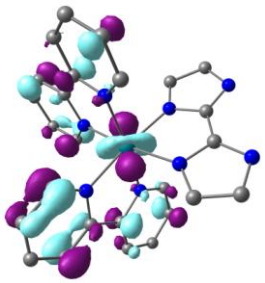
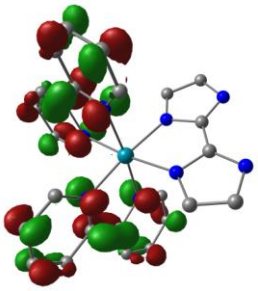
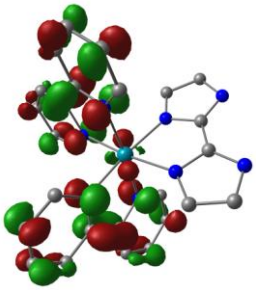
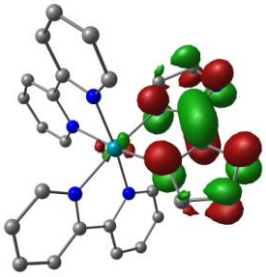
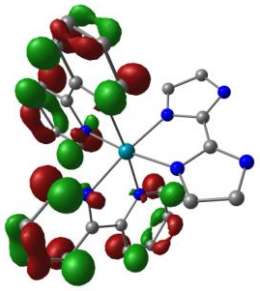
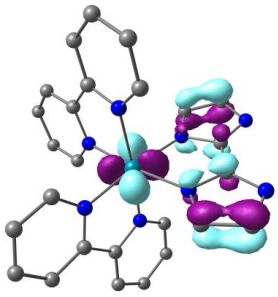
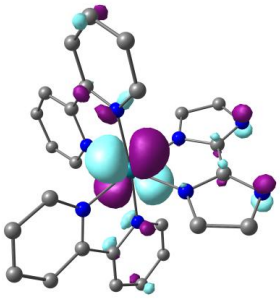
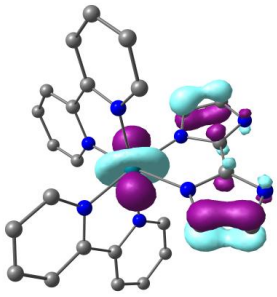
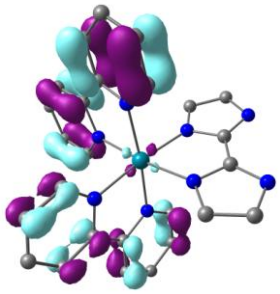
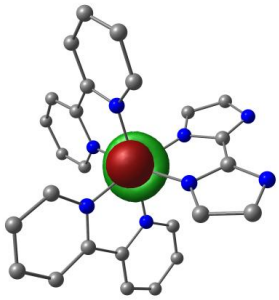
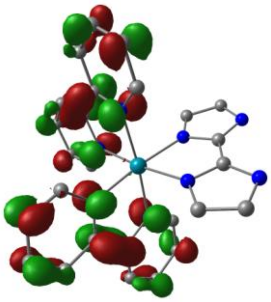
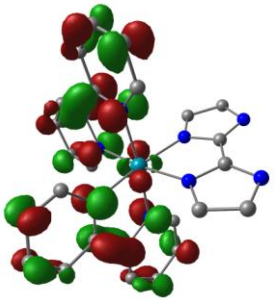
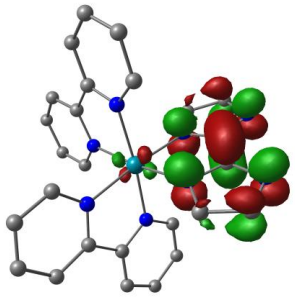
| α-spin | | | |
|---|---|---|---|
|  |  |  |  |
| SOMO | HOMO–1 | HOMO–2 | HOMO–3 |
|  |  |  |  |
| LUMO | LUMO+1 | LUMO+2 | LUMO+3 |
| β-spin | | | |
|  |  |  |  |
| HOMO | HOMO–1 | HOMO–2 | HOMO–3 |
|  |  |  |  |
| LUMO | LUMO+1 | LUMO+2 | LUMO+3 |

**Table S5** Selected molecular orbitals along with their energies and compositions of $\mathbf{2}^{2+}$ in *S*=0 state

| MO | Energy(eV) | Composition | | |
|---|---|---|---|---|
| | | Os | $H_2L_2$ | bpy |
| HOMO–5 | –12.028 | 0.01 | 0.17 | 0.81 |
| HOMO–4 | –12.005 | 0.00 | 0.58 | 0.42 |
| HOMO–3 | –10.781 | 0.29 | 0.62 | 0.09 |
| HOMO–2 | –10.556 | 0.62 | 0.20 | 0.18 |
| HOMO–1 | –10.525 | 0.72 | 0.13 | 0.15 |
| HOMO | –10.140 | 0.56 | 0.34 | 0.10 |
| LUMO | –7.367 | 0.03 | 0.22 | 0.75 |
| LUMO+1 | –7.170 | 0.08 | 0.12 | 0.80 |
| LUMO+2 | –6.862 | 0.09 | 0.66 | 0.24 |
| LUMO+3 | –6.390 | 0.05 | 0.03 | 0.92 |
| LUMO+4 | –6.184 | 0.03 | 0.04 | 0.92 |
| LUMO+5 | –6.114 | 0.04 | 0.01 | 0.94 |

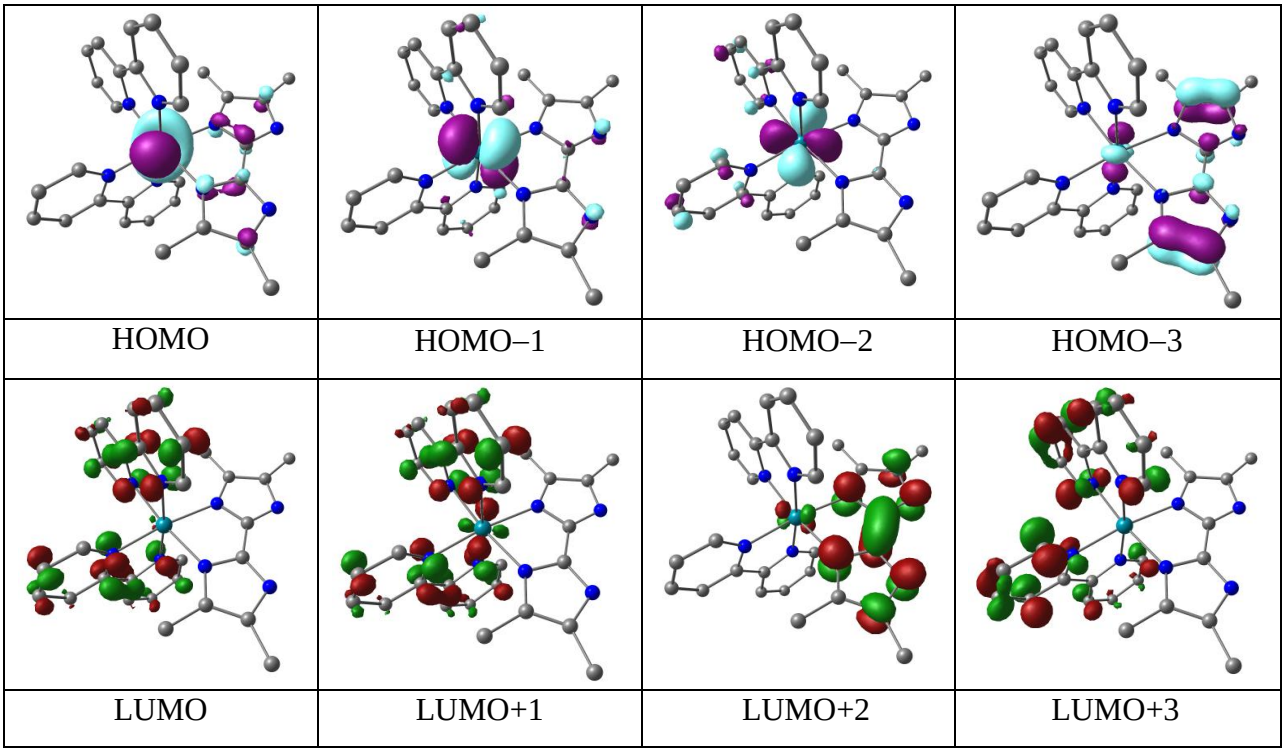


**Table S6** Selected molecular orbitals along with their energies and compositions of $\mathbf{2}^{3+}$ in *S*=1/2 state

| MO | Energy(eV) | Composition | | |
|---|---|---|---|---|
| | | Os | $H_2L_2$ | bpy |
| | | α-spin | | |
| HOMO–5 | –15.497 | 0.01 | 0.94 | 0.06 |
| HOMO–4 | –15.151 | 0.11 | 0.02 | 0.86 |
| HOMO–3 | –15.147 | 0.04 | 0.07 | 0.90 |
| HOMO–2 | –14.896 | 0.68 | 0.13 | 0.19 |
| HOMO–1 | –14.868 | 0.67 | 0.04 | 0.28 |
| SOMO | –13.943 | 0.03 | 0.97 | 0.97 |
| LUMO | –10.492 | 0.04 | 0.02 | 0.93 |
| LUMO+1 | –10.421 | 0.07 | 0.01 | 0.91 |
| LUMO+2 | –9.836 | 0.05 | 0.90 | 0.05 |
| LUMO+3 | –9.482 | 0.04 | 0.03 | 0.96 |
| LUMO+4 | –9.342 | 0.02 | 0.01 | 0.98 |
| LUMO+5 | –9.267 | 0.01 | 0.01 | 0.93 |
| | | β-spin | | |
| HOMO–5 | –15.436 | 0.00 | 0.93 | 0.07 |
| HOMO–4 | –15.173 | 0.02 | 0.01 | 0.97 |
| HOMO–3 | –15.134 | 0.01 | 0.08 | 0.91 |
| HOMO–2 | –14.618 | 0.71 | 0.12 | 0.16 |
| HOMO–1 | –14.615 | 0.70 | 0.06 | 0.24 |
| HOMO | –13.947 | 0.10 | 0.88 | 0.03 |
| LUMO | –12.374 | 0.72 | 0.14 | 0.14 |
| LUMO+1 | –10.479 | 0.04 | 0.02 | 0.93 |
| LUMO+2 | –10.389 | 0.08 | 0.01 | 0.90 |
| LUMO+3 | –9.773 | 0.05 | 0.90 | 0.05 |
| LUMO+4 | –9.474 | 0.04 | 0.03 | 0.93 |
| LUMO+5 | –9.286 | 0.04 | 0.01 | 0.94 |

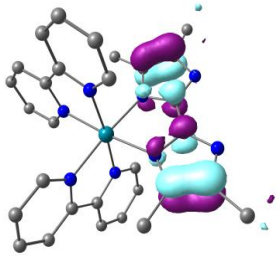
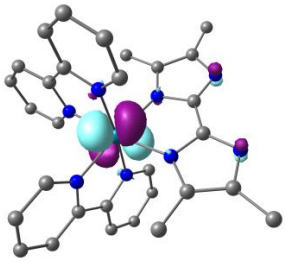
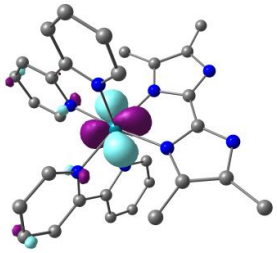
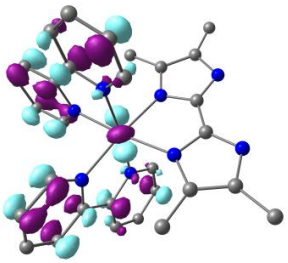
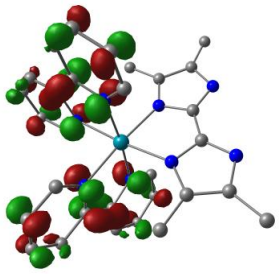
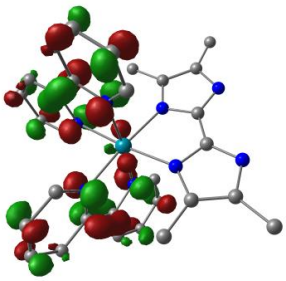
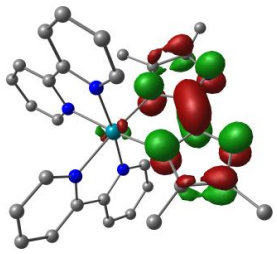
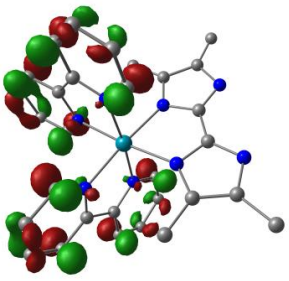
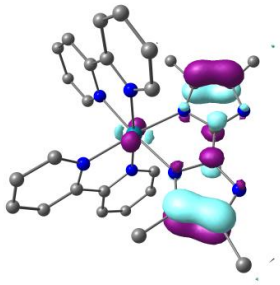
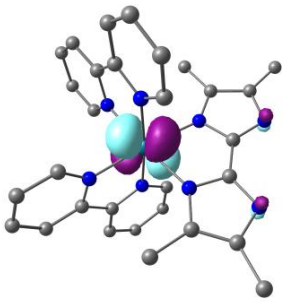
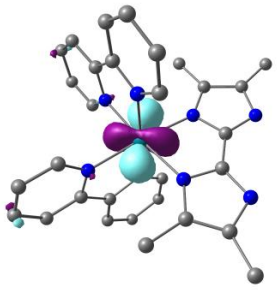
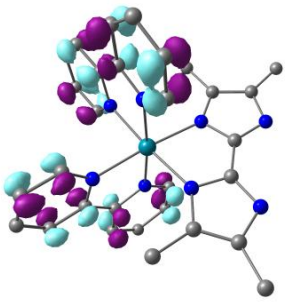
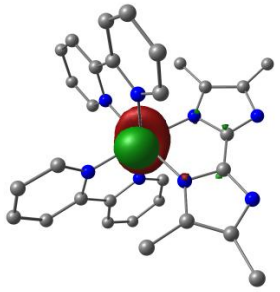
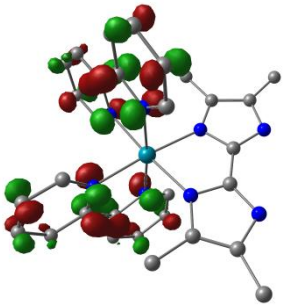
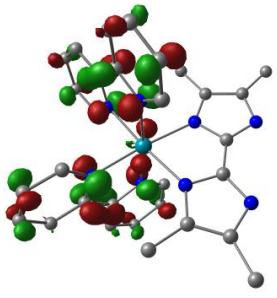
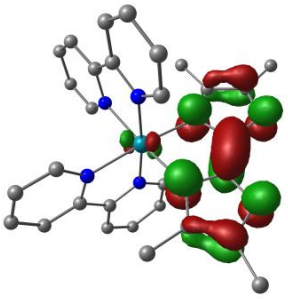
| α-spin | | | |
|---|---|---|---|
|  |  |  |  |
| SOMO | HOMO–1 | HOMO–2 | HOMO–3 |
|  |  |  |  |
| LUMO | LUMO+1 | LUMO+2 | LUMO+3 |
| β-spin | | | |
|  |  |  |  |
| HOMO | HOMO–1 | HOMO–2 | HOMO–3 |
|  |  |  |  |
| LUMO | LUMO+1 | LUMO+2 | LUMO+3 |

**Table S7** Selected molecular orbitals along with their energies and compositions of $\mathbf{3}^{2+}$ in *S*=0 state

| MO | Energy(eV) | Composition | | |
|---|---|---|---|---|
| | | Os | $L_1$ | bpy |
| HOMO–5 | –9.756 | 0.64 | 0.15 | 0.21 |
| HOMO–4 | –9.475 | 0.58 | 0.19 | 0.23 |
| HOMO–3 | –9.373 | 0.70 | 0.12 | 0.17 |
| HOMO–2 | –9.114 | 0.66 | 0.18 | 0.16 |
| HOMO–1 | –8.595 | 0.29 | 0.49 | 0.22 |
| HOMO | –8.473 | 0.10 | 0.60 | 0.30 |
| LUMO | –6.726 | 0.10 | 0.12 | 0.77 |
| LUMO+1 | –6.495 | 0.08 | 0.12 | 0.80 |
| LUMO+2 | –6.368 | 0.09 | 0.04 | 0.87 |
| LUMO+3 | –6.238 | 0.15 | 0.21 | 0.64 |
| LUMO+4 | –6.180 | 0.18 | 0.18 | 0.64 |
| LUMO+5 | –5.806 | 0.08 | 0.06 | 0.86 |

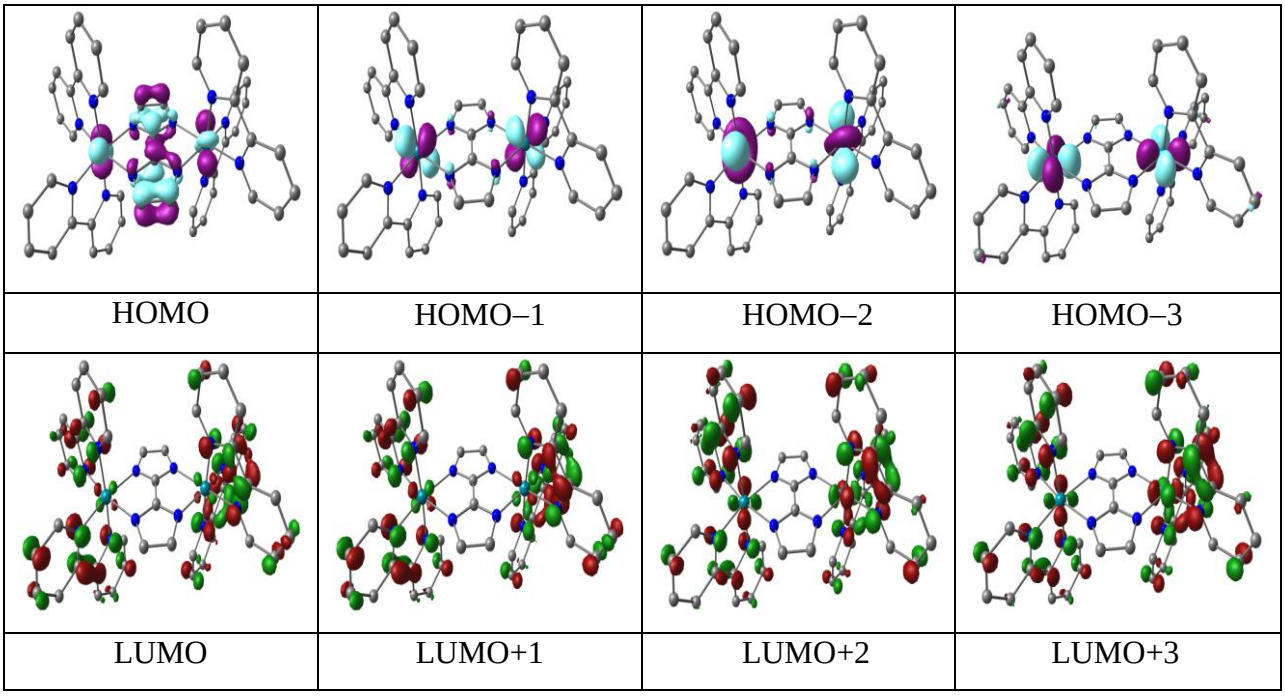


**Table S8** Selected molecular orbitals along with their energies and compositions of $\mathbf{3}^{3+}$ in *S*=1/2 state

| MO | Energy(eV) | Composition | | |
|---|---|---|---|---|
| | | Os | $L_1$ | bpy |
| | | α-spin | | |
| HOMO–5 | –12.609 | 0.75 | 0.09 | 0.17 |
| HOMO–4 | –12.598 | 0.75 | 0.06 | 0.19 |
| HOMO–3 | –12.510 | 0.71 | 0.06 | 0.23 |
| HOMO–2 | –12.430 | 0.74 | 0.05 | 0.21 |
| HOMO–1 | –12.280 | 0.71 | 0.12 | 0.17 |
| SOMO | –12.251 | 0.30 | 0.64 | 0.06 |
| LUMO | –8.873 | 0.05 | 0.02 | 0.93 |
| LUMO+1 | –8.847 | 0.06 | 0.01 | 0.92 |
| LUMO+2 | –8.786 | 0.09 | 0.02 | 0.89 |
| LUMO+3 | –8.757 | 0.09 | 0.01 | 0.90 |
| LUMO+4 | –7.933 | 0.05 | 0.03 | 0.92 |
| LUMO+5 | –7.910 | 0.04 | 0.02 | 0.94 |
| | | β-spin | | |
| HOMO–5 | –12.637 | 0.51 | 0.33 | 0.16 |
| HOMO–4 | –12.464 | 0.75 | 0.05 | 0.19 |
| HOMO–3 | –12.385 | 0.71 | 0.06 | 0.23 |
| HOMO–2 | –12.157 | 0.55 | 0.28 | 0.16 |
| HOMO–1 | –12.152 | 0.71 | 0.12 | 0.17 |
| HOMO | –11.605 | 0.77 | 0.08 | 0.16 |
| LUMO | –10.896 | 0.59 | 0.30 | 0.11 |
| LUMO+1 | –8.868 | 0.06 | 0.01 | 0.93 |
| LUMO+2 | –8.842 | 0.07 | 0.01 | 0.92 |
| LUMO+3 | –8.773 | 0.10 | 0.02 | 0.88 |
| LUMO+4 | –8.745 | 0.09 | 0.01 | 0.89 |
| LUMO+5 | –7.929 | 0.05 | 0.02 | 0.93 |

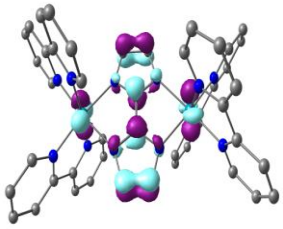
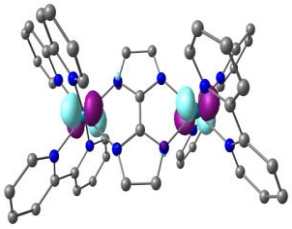
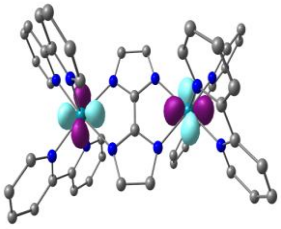
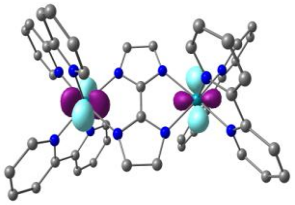
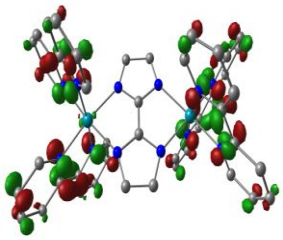
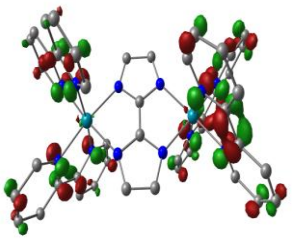
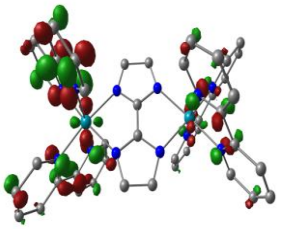
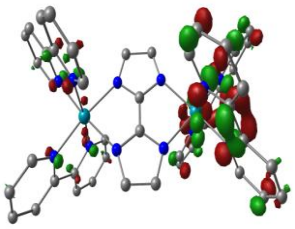
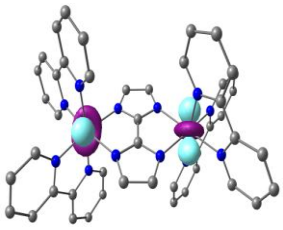
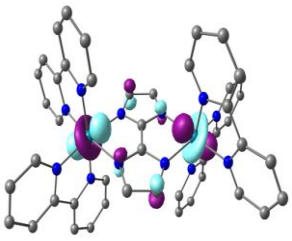
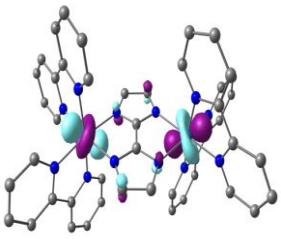
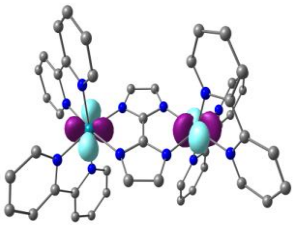
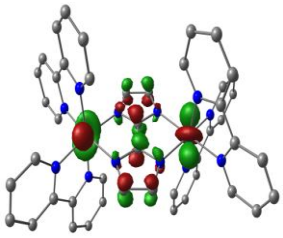
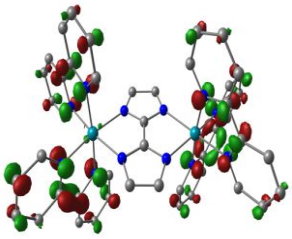
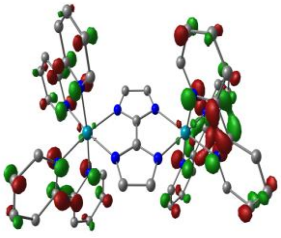
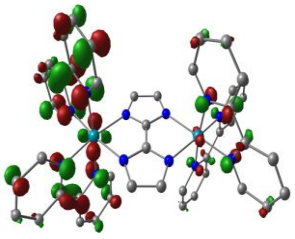
| α-spin | | | |
|---|---|---|---|
|  |  |  |  |
| SOMO | HOMO–1 | HOMO–2 | HOMO–3 |
|  |  |  |  |
| LUMO | LUMO+1 | LUMO+2 | LUMO+3 |
| β-spin | | | |
|  |  |  |  |
| HOMO | HOMO–1 | HOMO–2 | HOMO–3 |
|  |  |  |  |
| LUMO | LUMO+1 | LUMO+2 | LUMO+3 |

**Table S9** Selected molecular orbitals along with their energies and compositions of $\mathbf{3}^{4+}$ in $S$=1 state ($E_{S1}$-$E_{S0}$= 1588 $cm^{-1}$)

| MO | Energy(eV) | Composition | | |
|---|---|---|---|---|
| | | Os | $L_1$ | bpy |
| | | α-spin | | |
| HOMO–5 | –16.087 | 0.20 | 0.04 | 0.76 |
| HOMO–4 | –16.075 | 0.62 | 0.07 | 0.31 |
| HOMO–3 | –15.897 | 0.69 | 0.06 | 0.25 |
| HOMO–2 | –15.733 | 0.70 | 0.03 | 0.27 |
| SOMO 2 | –15.590 | 0.69 | 0.15 | 0.17 |
| SOMO 1 | –14.801 | 0.06 | 0.93 | 0.01 |
| LUMO | –11.425 | 0.04 | 0.01 | 0.94 |
| LUMO+1 | –11.413 | 0.05 | 0.02 | 0.93 |
| LUMO+2 | –11.367 | 0.07 | 0.01 | 0.91 |
| LUMO+3 | –11.341 | 0.07 | 0.01 | 0.92 |
| LUMO+4 | –10.470 | 0.06 | 0.12 | 0.82 |
| LUMO+5 | –10.416 | 0.04 | 0.02 | 0.94 |
| | | β-spin | | |
| HOMO–5 | –16.080 | 0.01 | 0.00 | 0.99 |
| HOMO–4 | –15.635 | 0.72 | 0.07 | 0.21 |
| HOMO–3 | –15.567 | 0.71 | 0.07 | 0.22 |
| HOMO–2 | –15.496 | 0.71 | 0.06 | 0.23 |
| HOMO–1 | –15.309 | 0.71 | 0.14 | 0.16 |
| HOMO | –14.775 | 0.24 | 0.68 | 0.07 |
| LUMO | –13.341 | 0.77 | 0.07 | 0.15 |
| LUMO+1 | –13.172 | 0.66 | 0.22 | 0.12 |
| LUMO+2 | –11.412 | 0.04 | 0.01 | 0.94 |
| LUMO+3 | –11.398 | 0.05 | 0.02 | 0.93 |
| LUMO+4 | –11.342 | 0.08 | 0.01 | 0.91 |
| LUMO+5 | –11.317 | 0.08 | 0.01 | 0.91 |

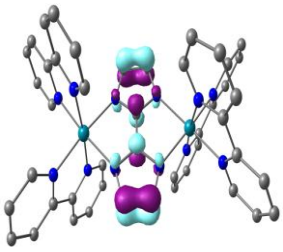
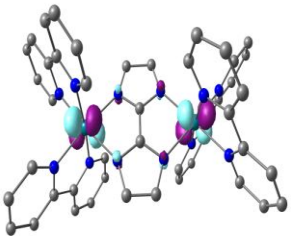
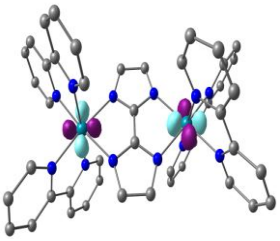
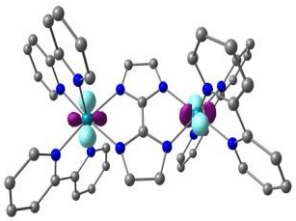
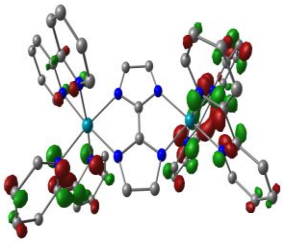
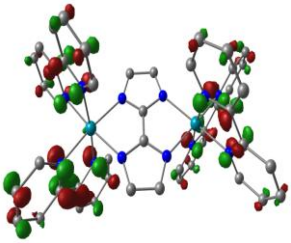
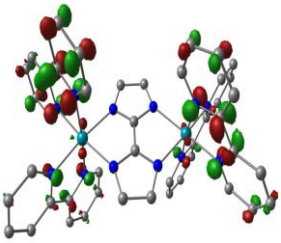
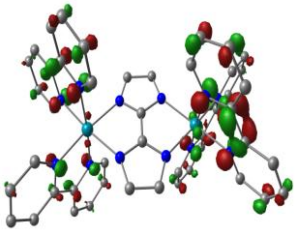
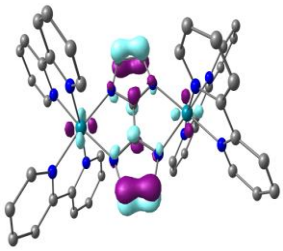
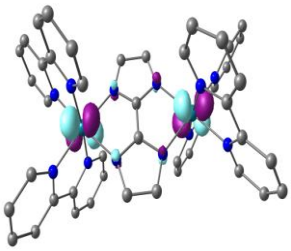
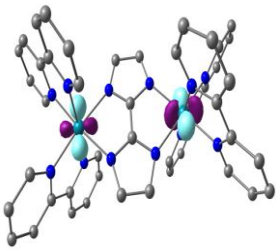
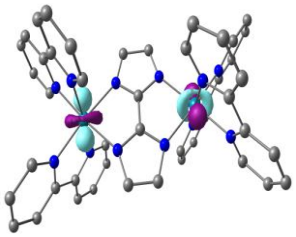
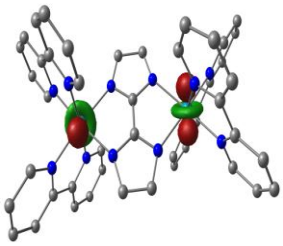
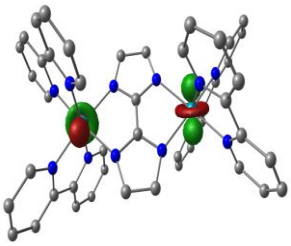
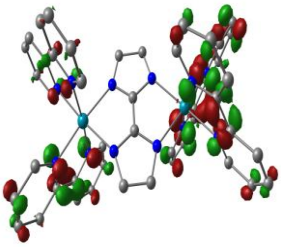
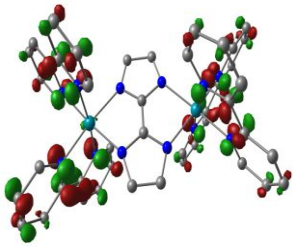
| α-spin | | | |
|---|---|---|---|
|  |  |  |  |
| SOMO 1 | SOMO 2 | HOMO–2 | HOMO–3 |
|  |  |  |  |
| LUMO | LUMO+1 | LUMO+2 | LUMO+3 |
| β-spin | | | |
|  |  |  |  |
| HOMO | HOMO–1 | HOMO–2 | HOMO–3 |
|  |  |  |  |
| LUMO | LUMO+1 | LUMO+2 | LUMO+3 |

**Table S10** Selected molecular orbitals along with their energies and compositions of $\mathbf{4}^{2+}$ in *S*=0 state

| MO | Energy(eV) | Composition | | |
|---|---|---|---|---|
| | | Os | $L_2$ | bpy |
| HOMO–5 | –9.575 | 0.72 | 0.08 | 0.20 |
| HOMO–4 | –9.325 | 0.71 | 0.09 | 0.21 |
| HOMO–3 | –9.268 | 0.58 | 0.30 | 0.12 |
| HOMO–2 | –8.987 | 0.37 | 0.52 | 0.11 |
| HOMO–1 | –8.878 | 0.38 | 0.52 | 0.09 |
| HOMO | –7.494 | 0.02 | 0.95 | 0.03 |
| LUMO | –6.479 | 0.07 | 0.02 | 0.91 |
| LUMO+1 | –6.341 | 0.11 | 0.02 | 0.88 |
| LUMO+2 | –6.281 | 0.08 | 0.02 | 0.90 |
| LUMO+3 | –6.127 | 0.10 | 0.02 | 0.88 |
| LUMO+4 | –5.591 | 0.04 | 0.03 | 0.93 |
| LUMO+5 | –5.416 | 0.04 | 0.02 | 0.94 |

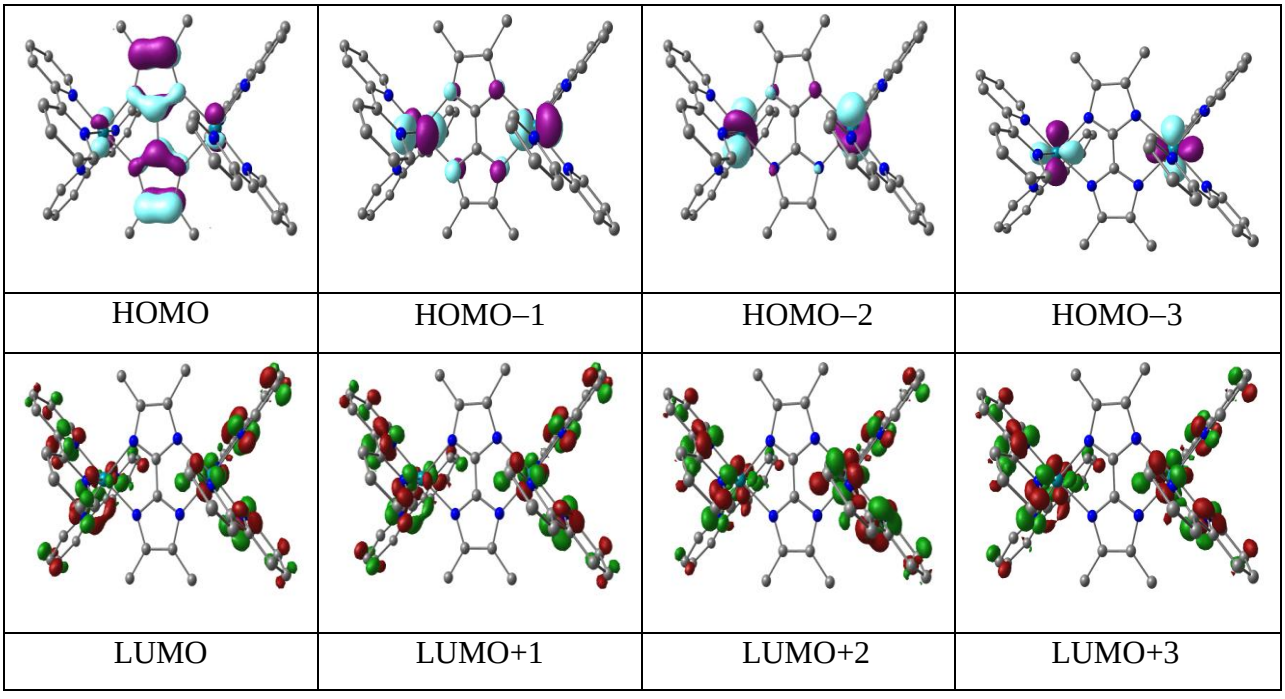


**Table S11** Selected molecular orbitals along with their energies and compositions of $\mathbf{4}^{3+}$ in *S*=1/2 state

| MO | Energy(eV) | Composition | | |
|---|---|---|---|---|
| | | Os | $L_2$ | bpy |
| | | α-spin | | |
| HOMO–5 | –12.335 | 0.75 | 0.05 | 0.19 |
| HOMO–4 | –12.249 | 0.71 | 0.07 | 0.22 |
| HOMO–3 | –12.188 | 0.76 | 0.09 | 0.15 |
| HOMO–2 | –12.118 | 0.73 | 0.06 | 0.21 |
| HOMO–1 | –11.989 | 0.71 | 0.13 | 0.17 |
| SOMO | –11.959 | 0.35 | 0.59 | 0.07 |
| LUMO | –8.759 | 0.05 | 0.02 | 0.93 |
| LUMO+1 | –8.732 | 0.07 | 0.02 | 0.92 |
| LUMO+2 | –8.660 | 0.10 | 0.02 | 0.88 |
| LUMO+3 | –8.625 | 0.10 | 0.01 | 0.89 |
| LUMO+4 | –7.839 | 0.06 | 0.04 | 0.89 |
| LUMO+5 | –7.806 | 0.04 | 0.03 | 0.93 |
| | | β-spin | | |
| HOMO–5 | –12.301 | 0.60 | 0.21 | 0.18 |
| HOMO–4 | –12.241 | 0.75 | 0.06 | 0.19 |
| HOMO–3 | –12.165 | 0.71 | 0.05 | 0.23 |
| HOMO–2 | –11.936 | 0.64 | 0.20 | 0.17 |
| HOMO–1 | –11.898 | 0.70 | 0.13 | 0.17 |
| HOMO | –11.563 | 0.76 | 0.09 | 0.15 |
| LUMO | –10.658 | 0.37 | 0.55 | 0.08 |
| LUMO+1 | –8.756 | 0.06 | 0.02 | 0.93 |
| LUMO+2 | –8.728 | 0.07 | 0.02 | 0.91 |
| LUMO+3 | –8.647 | 0.10 | 0.02 | 0.88 |
| LUMO+4 | –8.613 | 0.10 | 0.01 | 0.88 |
| LUMO+5 | –7.834 | 0.06 | 0.03 | 0.90 |

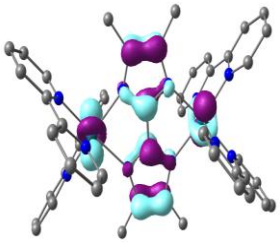
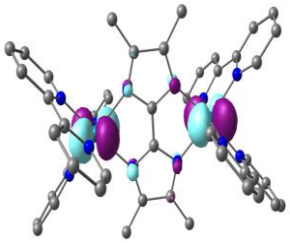
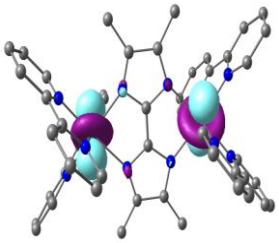
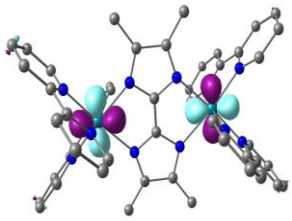
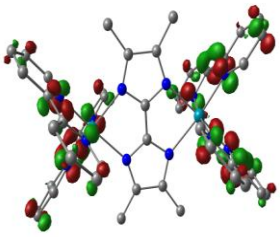
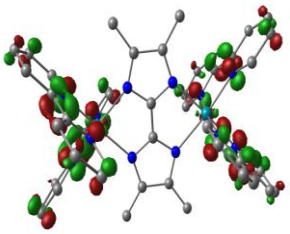
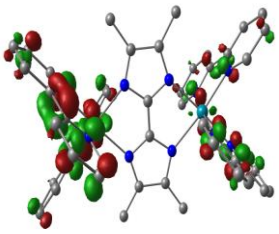
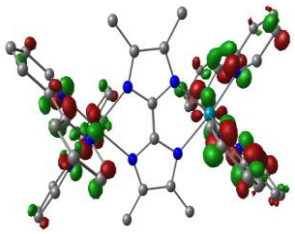
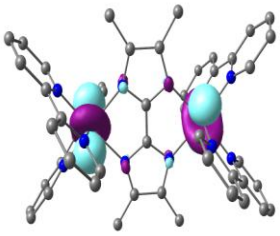
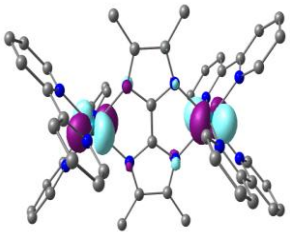
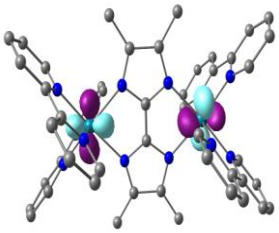
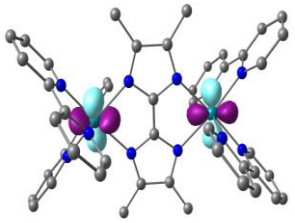
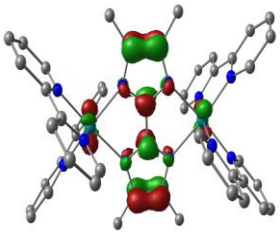
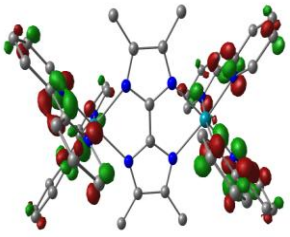
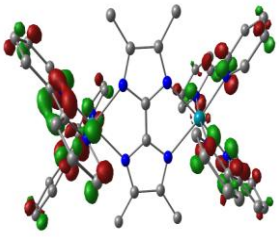
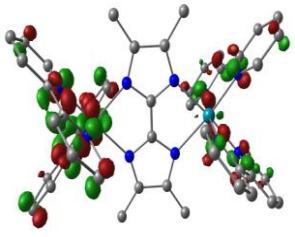
| α-spin | | | |
|---|---|---|---|
|  |  |  |  |
| SOMO | HOMO–1 | HOMO–2 | HOMO–3 |
|  |  |  |  |
| LUMO | LUMO+1 | LUMO+2 | LUMO+3 |
| β-spin | | | |
|  |  |  |  |
| HOMO | HOMO–1 | HOMO–2 | HOMO–3 |
|  |  |  |  |
| LUMO | LUMO+1 | LUMO+2 | LUMO+3 |

**Table S12** Selected molecular orbitals along with their energies and compositions of $\mathbf{4}^{4+}$ in $S$=1 state ($E_{S1}$-$E_{S0}$= 1421 $cm^{-1}$)

| MO | Energy(eV) | Composition | | |
|---|---|---|---|---|
| | | Os | $L_2$ | bpy |
| | | α-spin | | |
| HOMO–5 | –15.756 | 0.62 | 0.11 | 0.27 |
| HOMO–4 | –15.553 | 0.71 | 0.07 | 0.22 |
| HOMO–3 | –15.385 | 0.70 | 0.05 | 0.25 |
| HOMO–2 | –15.318 | 0.73 | 0.03 | 0.24 |
| SOMO 2 | –15.213 | 0.70 | 0.14 | 0.15 |
| SOMO 1 | –14.385 | 0.05 | 0.94 | 0.01 |
| LUMO | –11.269 | 0.04 | 0.02 | 0.94 |
| LUMO+1 | –11.259 | 0.05 | 0.02 | 0.93 |
| LUMO+2 | –11.193 | 0.08 | 0.02 | 0.91 |
| LUMO+3 | –11.167 | 0.07 | 0.01 | 0.92 |
| LUMO+4 | –10.344 | 0.06 | 0.22 | 0.72 |
| LUMO+5 | –10.278 | 0.05 | 0.02 | 0.93 |
| | | β-spin | | |
| HOMO–5 | –15.850 | 0.09 | 0.74 | 0.17 |
| HOMO–4 | –15.314 | 0.72 | 0.09 | 0.19 |
| HOMO–3 | –15.168 | 0.74 | 0.04 | 0.22 |
| HOMO–2 | –15.165 | 0.72 | 0.05 | 0.23 |
| HOMO–1 | –14.964 | 0.71 | 0.14 | 0.15 |
| HOMO | –14.302 | 0.50 | 0.38 | 0.11 |
| LUMO | –13.311 | 0.77 | 0.08 | 0.15 |
| LUMO+1 | –12.862 | 0.37 | 0.56 | 0.07 |
| LUMO+2 | –11.259 | 0.05 | 0.02 | 0.94 |
| LUMO+3 | –11.248 | 0.05 | 0.02 | 0.93 |
| LUMO+4 | –11.166 | 0.09 | 0.02 | 0.90 |
| LUMO+5 | –11.142 | 0.08 | 0.01 | 0.90 |

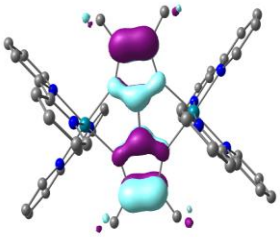
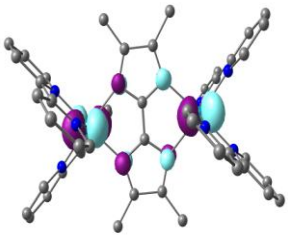
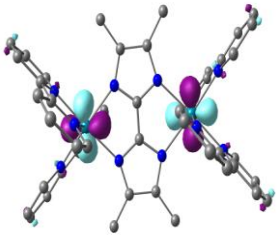
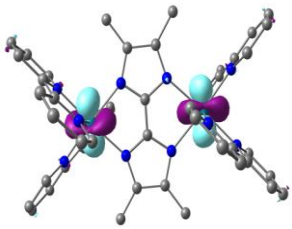
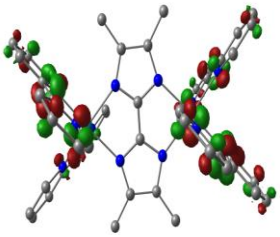
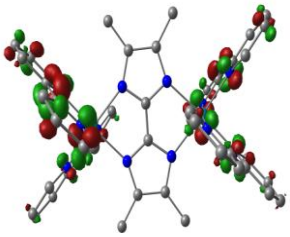
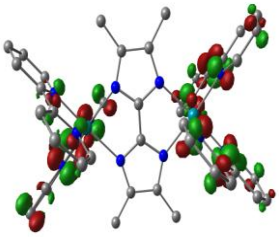
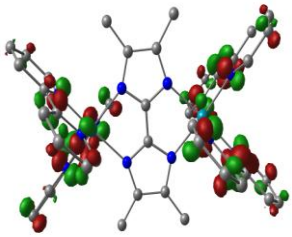
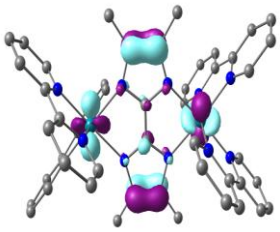
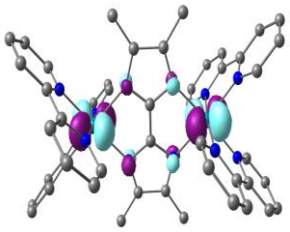
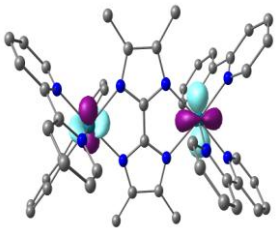
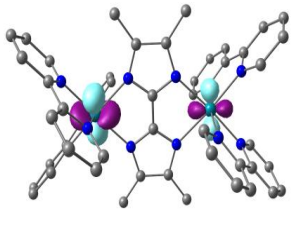
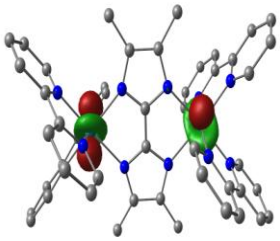
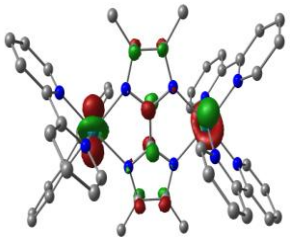
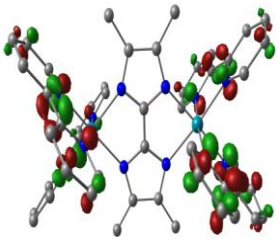
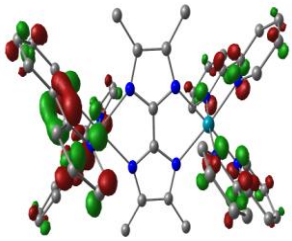
| α-spin | | | |
|---|---|---|---|
|  |  |  |  |
| SOMO 1 | SOMO 2 | HOMO–2 | HOMO–3 |
|  |  |  |  |
| LUMO | LUMO+1 | LUMO+2 | LUMO+3 |
| β-spin | | | |
|  |  |  |  |
| HOMO | HOMO–1 | HOMO–2 | HOMO–3 |
|  |  |  |  |
| LUMO | LUMO+1 | LUMO+2 | LUMO+3 |

**Table S13** Experimental and TD-DFT ((U)B3LYP/CPCM/$CH_3CN$) calculated electronic transitions for $\mathbf{1}^n$ and $\mathbf{2}^n$

| $\lambda$/nm (exp) ($\varepsilon$/dm$^3$mol$^{-1}$cm$^{-1}$) | $\lambda$/ nm (DFT) ($f$) | Transition | Character |
|---|---|---|---|
| | | $\mathbf{1}^{2+}$($S$=0) | |
| 665(2480) | 583(0.003) | HOMO→LUMO(0.70) | Os(dπ)→bpy(π*) |
| 498(10620) | 507(0.012) | HOMO-2→LUMO(0.50) | Os(dπ)/bpy(π)→bpy(π*) |
| 448(9360) | 429(0.002) | HOMO→LUMO+3(0.69) | Os(dπ)→bpy(π*) |
| 400(9410) | 394(0.009) | HOMO→LUMO+3(0.69) | Os(dπ)→bpy(π*) |
| 370(10910) | 358(0.054) | HOMO-2→LUMO+3(0.64) | Os(dπ)/bpy(π)→bpy(π*) |
| 345(10810) | 290(0.060) | HOMO-4→LUMO(0.66) | bpy(π)→bpy(π*) |
| 292(67960) | 275(0.289) | HOMO-3→LUMO+3(0.53) | $H_2L_1$(π)→bpy(π*) |
| 244(28310) | 235(0.062) | HOMO-4→LUMO+9(0.42) | bpy(π)→bpy(π*) |
| | | HOMO-5→LUMO+5(0.29) | bpy(π)→bpy(π*) |
| | | $\mathbf{1}^{3+}$($S$=1/2) | |
| 490(4230) | 568(0.003) | HOMO-3(β)→LUMO(β)(0.99) | bpy(π)→Os(dπ) |
| 450(4220) | 403(0.004) | HOMO-4(β)→LUMO(β)(0.99) | $H_2L_1$(π)→Os(dπ) |
| 364(8170) | 391(0.019) | HOMO-2(β)→LUMO+1(β)(0.54) | $H_2L_1$(π)/Os(dπ)→bpy(π*) |
| 315(18240) | 296(0.053) | HOMO-4(β)→LUMO+1(β)(0.75) | bpy(π)→bpy(π*) |
| 285(44820) | 294(0.103) | HOMO-4(α)→LUMO+1(α)(0.71) | bpy(π)→bpy(π*) |
| 248(31080) | 256(0.079) | HOMO-7(β)→LUMO+1(β)(0.22) | bpy(π)→bpy(π*) |
| | | HOMO-3(α)→LUMO+2(α)(0.21) | bpy(π)→$H_2L_1$(π*) |
| | | HOMO-8(β)→LUMO+2(β)(0.20) | bpy(π)→bpy(π*) |
| | | $\mathbf{2}^{2+}$($S$=0) | |
| 698(2600) | 603(0.005) | HOMO→LUMO(0.69) | Os(dπ)/$H_2L_2$(π)→bpy(π*)/$H_2L_2$(π*) |
| 535(6400) | 519(0.004) | HOMO-1→LUMO(0.67) | Os(dπ)/bpy(π)→bpy(π*)/$H_2L_2$(π*) |
| 508(10450) | 515(0.006) | HOMO-1→LUMO+1(0.53) | Os(dπ)/bpy(π)→bpy(π*)/$H_2L_2$(π*) |
| 410(10490) | 372(0.022) | HOMO→LUMO+6(0.62) | Os(dπ)/$H_2L_2$(π)→bpy(π*) |
| 345(13570) | 302(0.030) | HOMO-3→LUMO+3(0.68) | $H_2L_2$(π)/Os(dπ)→bpy(π*) |
| 294(55790) | 277(0.675) | HOMO-4→LUMO+1(0.56) | $H_2L_2$(π)/bpy(π)→bpy(π*)/$H_2L_2$(π*) |
| 244(25210) | 268(0.080) | HOMO-6→LUMO+1(0.66) | bpy(π)→bpy(π*)/$H_2L_2$(π*) |
| | | $\mathbf{2}^{3+}$($S$=1/2) | |
| 652(1910) | 552(0.006) | HOMO-3(β)→LUMO(β)(0.99) | bpy(π)→Os(dπ)/bpy(π*) |
| 496(7050) | 503(0.011) | HOMO-5(β)→LUMO(β)(0.99) | $H_2L_2$(π)→Os(dπ)/bpy(π*) |
| 405(7950) | 397(0.015) | HOMO-2(β)→LUMO+1(β)(0.57) | Os(dπ)/$H_2L_2$(π)→bpy(π*) |
| 315(20820) | 317(0.020) | HOMO(β)→LUMO+4(β)(0.60) | $H_2L_2$(π)→bpy(π*) |
| 294(48860) | 298(0.151) | HOMO-4(β)→LUMO+1(β)(0.48) | bpy(π)→bpy(π*) |
| | | SOMO(α)→LUMO+2(α)(0.13) | $H_2L_2$(π)→$H_2L_2$(π*) |
| 244(25780) | 246(0.115) | HOMO-3(α)→LUMO+3(α)(0.67) | bpy(π)→bpy(π*) |

**Table S14** Experimental and TD-DFT ((U)B3LYP/CPCM/$CH_3CN$) calculated electronic transitions for $\mathbf{3}^n$ and $\mathbf{4}^n$

| $\lambda$/nm (exp) ($\varepsilon$/dm$^3$mol$^{-1}$cm$^{-1}$) | $\lambda$/ nm (DFT) ($f$) | Transition | Character |
|---|---|---|---|
| | | $\mathbf{3}^{2+}$($S$=0) | |
| 674(7220) | 569(0.010) | HOMO-1→LUMO(0.55) | $L_1(\pi)$/Os(dπ)→bpy(π*)/$L_1$(π*) |
| 522(24060) | 508(0.092) | HOMO-3→LUMO(0.44) | Os(dπ)/bpy(π)→bpy(π*) |
| | | HOMO-2→LUMO+1(0.44) | Os(dπ)/$L_1$(π)→bpy(π*) |
| 489(25120) | 482(0.063) | HOMO-3→LUMO+2(0.47) | Os(dπ)/bpy(π)→bpy(π*) |
| | | HOMO-2→LUMO+3(0.28) | Os(dπ)/$L_1$(π)→bpy(π*) |
| 428(24780) | 373(0.040) | HOMO-2→LUMO+5(0.33) | Os(dπ)/$L_1$(π)→bpy(π*) |
| | | HOMO-1→LUMO+6(0.28) | $L_1(\pi)$/Os(dπ)→bpy(π*) |
| 346(27430) | 369(0.182) | HOMO-1→LUMO+7(0.44) | $L_1(\pi)$/Os(dπ)→bpy(π*) |
| | | HOMO→LUMO+9(0.20) | $L_1(\pi)$/bpy(π)→bpy(π*) |
| 292(136540) | 273(0.883) | HOMO-8→LUMO+2(0.32) | bpy(π)→bpy(π*) |
| | | HOMO-10→LUMO(0.23) | bpy(π)→bpy(π*)/$L_1$(π*) |
| 244(75420) | 232(0.198) | HOMO-13→LUMO+3(0.34) | $L_1(\pi)$/bpy(π)→bpy(π*)/$L_1$(π*) |
| | | HOMO-8→LUMO+6(0.29) | bpy(π)→bpy(π*) |
| | | $\mathbf{3}^{3+}$($S$=1/2) | |
| 1152(1400) | 1264(0.0001) | HOMO-5(β)→LUMO(β)(0.94) | Os(dπ)/$L_1$(π)→Os(dπ)/$L_1$(π*) |
| 669(6100) | 617(0.002) | HOMO(β)→LUMO+1(β)(0.89) | Os(dπ)/bpy(π)→bpy(π*) |
| 510(20050) | 526(0.003) | HOMO-3(β)→LUMO+1(β)(0.37) | Os(dπ)/bpy(π)→bpy(π*) |
| | | HOMO-2(β)→LUMO+2(β)(0.26) | Os(dπ)/$L_1$(π)→bpy(π*) |
| 483(20980) | 484(0.009) | HOMO-1(α)→LUMO(α)(0.57) | Os(dπ)/bpy(π)→bpy(π*) |
| 380(24030) | 387(0.010) | HOMO-7(β)→LUMO+3(β)(0.16) | bpy(π)→bpy(π*) |
| | | HOMO-10(α)→LUMO(α)(0.16) | bpy(π)→bpy(π*) |
| 344(24870) | 332(0.053) | HOMO-14(β)→LUMO+1(β)(0.56) | bpy(π)/$L_1$(π)→Os(dπ)/$L_1$(π*) |
| 292(128060) | 279(0.126) | HOMO-8(α)→LUMO+1(α)(0.45) | bpy(π)→bpy(π*) |
| | | HOMO-7(α)→LUMO+2(α)(0.42) | bpy(π)→bpy(π*) |
| 244(75500) | 267(0.066) | HOMO-10(α)→LUMO+4(β)(0.52) | $L_1$(π)→bpy(π*) |
| | | $\mathbf{3}^{4+}$($S$=1) | |
| 1152(1790) | (NR) | | |
| 664(5310) | 657(0.008) | HOMO-3(β)→LUMO+1(β)(0.63) | Os(dπ)/bpy(π)→Os(dπ)/$L_1$(π*) |
| 509(16540) | 460(0.007) | SOMO 1(α)→LUMO+2(α)( (0.44) | $L_1(\pi)$/Os(dπ)→bpy(π*) |
| 478(18300) | 421(0.007) | SOMO 2(α)→LUMO+5(α)(0.58) | Os(dπ)/bpy(π)→bpy(π*) |
| 372(22270) | 316(0.028) | HOMO-11(β)→LUMO(β)(0.54) | bpy(π)→Os(dπ)/bpy(π*) |
| 342(23390) | 346(0.040) | HOMO-12(β)→LUMO(β)(0.71) | bpy(π)/$L_1$(π)→Os(dπ)/bpy(π*) |
| 292(121110) | 290(0.135) | HOMO-7(α)→LUMO+1(α)(0.28) | bpy(π)→bpy(π*) |
| | | HOMO-6(α)→LUMO+3(α)(0.23) | bpy(π)→bpy(π*) |
| 244(75900) | 249(0.104) | HOMO-5(α)→LUMO+4(α)(0.59) | bpy(π)→bpy(π*) |

| | | | |
|---|---|---|---|
| | | $\mathbf{4}^{2+}$($S$=0) | |
| 678(5520) | 588(0.009) | HOMO-2→LUMO+1(0.38) | $L_2(\pi)$/Os(dπ)→bpy(π*) |
| | | HOMO-3→LUMO(0.35) | Os(dπ)/$L_2(\pi)$→bpy(π*) |
| 511(19200) | 556(0.012) | HOMO-2→LUMO+3(0.48) | $L_2(\pi)$/Os(dπ)→bpy(π*) |
| | | HOMO-6→LUMO+2(0.14) | Os(dπ)/bpy(π)→bpy(π*) |
| 434(18600) | 412(0.050) | HOMO→LUMO+9(0.65) | $L_2(\pi)$→bpy(π*) |
| 345(21430) | 324(0.010) | HOMO→LUMO+12(0.66) | $L_2(\pi)$→$L_2(\pi^*)$ |
| 292(97140) | 273(0.779) | HOMO-10→LUMO+2(0.31) | bpy(π)/$L_2(\pi)$→bpy(π*) |
| | | HOMO-11→LUMO+2(0.14) | bpy(π)/$L_2(\pi)$→bpy(π*) |
| 244(53890) | 234(0.155) | HOMO-11→LUMO+6(0.28) | bpy(π)/$L_2(\pi)$→bpy(π*) |
| | | HOMO-11→LUMO+7(0.22) | bpy(π)/$L_2(\pi)$→bpy(π*) |
| | | $\mathbf{4}^{3+}$($S$=1/2) | |
| 1087(1580) | 1319(0.002) | HOMO-3(β)→LUMO(β)(0.98) | Os(dπ)/bpy(π)→ $L_2(\pi^*)$/Os(dπ) |
| 662(5020) | 567(0.002) | HOMO-1(α)→LUMO+1(α)(0.24) | Os(dπ)/bpy(π)→bpy(π*) |
| | | HOMO(β)→LUMO+2(β)(0.21) | Os(dπ)/bpy(π)→bpy(π*) |
| 498(17090) | 472(0.025) | HOMO-2(α)→LUMO+1(α)(0.51) | Os(dπ)/bpy(π)→bpy(π*) |
| 416(17340) | 449(0.038) | HOMO-2(β)→LUMO+3(β)(0.55) | Os(dπ)/$L_2(\pi)$→bpy(π*) |
| 340(19990) | 292(0.059) | HOMO-8(α)→LUMO+1(α)(0.27) | bpy(π)→bpy(π*) |
| | | HOMO-21(β)→LUMO(β)(0.17) | bpy(π)→$L_2(\pi^*)$ |
| 292(93210) | 273(0.740) | HOMO-8(α)→LUMO+2(α)(0.43) | bpy(π)→bpy(π*) |
| | | HOMO-7(α)→LUMO+3(α)(0.13) | bpy(π)→bpy(π*) |
| 244(54280) | 252(0.069) | HOMO-6(β)→LUMO+6(β)(0.67) | $L_2(\pi)$/bpy(π)→bpy(π*) |
| | | $\mathbf{4}^{4+}$($S$=1) | |
| 1157(1950) | 1443(0.0001) | HOMO(β)→LUMO+1(β)(0.90) | Os(dπ)/$L_2(\pi)$→$L_2(\pi^*)$/Os(dπ) |
| 657(4440) | 759(0.003) | HOMO-4(β)→LUMO+1(β)(0.88) | Os(dπ)/bpy(π)→$L_2(\pi^*)$/Os(dπ) |
| 498(14800) | 437(0.008) | SOMO 2(β)→LUMO+5(α)(0.75) | Os(dπ)/bpy(π)→bpy(π*) |
| 410(15900) | 403(0.014) | SOMO 1(α)→LUMO+12(α)(0.62) | $L_2(\pi)$→bpy(π*) |
| 340(19010) | 320(0.045) | SOMO 1(α)→LUMO+1(α)(0.22) | $L_2(\pi)$→bpy(π*)/$L_2(\pi^*)$ |
| | | HOMO-19(β)→LUMO+3(β)(0.19) | bpy(π)/$L_2(\pi)$→$L_2(\pi^*)$ |
| 292(87960) | 282(0.095) | HOMO-8(β)→LUMO+3(β)(0.34) | bpy(π)→bpy(π*) |
| | | HOMO-7(β)→LUMO+3(β)(0.12) | bpy(π)→bpy(π*) |
| 244(54780) | 257(0.041) | HOMO-11(α)→LUMO+4(α)(0.21) | $L_2(\pi)$→bpy(π*)/$L_2(\pi^*)$ |
| | | HOMO-6(α)→LUMO+4(α)(0.19) | bpy(π)→bpy(π*)/$L_2(\pi^*)$ |

NR: Not resolved

**Table S15** DFT calculated structural parameters and NBO charges

| Complex | $X^-$ | d(N8-H8) Å | d(H8···X) Å | $\alpha$(N8-H8-X)º | $q_N$ | $q_X$ | $q_{Os}$ |
|---|---|---|---|---|---|---|---|
| $\mathbf{1}^{2+}/\mathbf{2}^{2+}$ | - | 1.011/ 1.011 | - | - | -0.528/ -0.528 | - | 0.340/ 0.347 |
| **A** | $F^-$ | 1.554/ 1.532 | 1.005/ 1.011 | 159.5/ 160.7 | -0.562/ -0.565 | -0.609/ -0.613 | 0.363/ 0.371 |
| **B** | $CN^-$ | 1.719/ 1.697 | 1.053/ 1.059 | 161.6/ 163.6 | -0.556/ -0.563 | -0.517/ -0.524 | 0.361/ 0.370 |
| **C** | $OAc^-$ | 1.710/ 1.690 | 1.017/ 1.022 | 170.4/ 169.4 | -0.560/ -0.565 | -0.537/ -0.545 | 0.365/ 0.374 |

**Table S16** Selected crystallographic parameters of **1**

| Compound | **1** |
|---|---|
| Formula | $C_{26}H_{20}N_8Os$ |
| $M_r$ | 634.70 |
| Radiation | $CuK_\alpha$ |
| Crystal system | Tetragonal |
| Space group | I 41/a |
| *a*/Å | 29.488(5) |
| *b*/Å | 29.488(5) |
| *c*/Å | 16.688(5) |
| $\alpha$ (°) | 90.000(5) |
| $\beta$ (°) | 90.000(5) |
| $\gamma$ (°) | 90.000(5) |
| *V*/Å$^3$ | 14511(7) |
| $\mu$/mm$^{-1}$ | 6.807 |
| *Z* | 16 |
| *T*/K | 150(2) |
| $\rho_{calcd}$/g cm$^{-3}$ | 1.162 |
| *F*(000) | 4928 |
| $\theta$ range (°) | 3.043 to 71.282 |
| Data/restraints/parameters | 6911/0/317 |
| R1, wR2 ($I>2\sigma(I)$) | 0.0490, 0.1460 |
| R1, wR2 (all data) | 0.0774, 0.1623 |
| GOF on $F^2$ | 0.930 |
| Largest diff. peak per hole/e Å$^{-3}$ | 0.606/-0.607 |

**Table S17** Experimental (X-ray) calculated selected bond distances (Å) and bond angles (°) for **1**

| Bond distances (Å) | X-ray | Bond angles (°) | X-ray |
|---|---|---|---|
| Os1-N1 | 2.050(6) | N1-Os1-N2 | 80.4(3) |
| Os1-N2 | 2.059(6) | N1-Os1-N3 | 94.6(3) |
| Os1-N3 | 2.067(7) | N1-Os1-N4 | 173.3(3) |
| Os1-N4 | 2.006(7) | N1-Os1-N5 | 92.2(2) |
| Os1-N5 | 2.105(7) | N1-Os1-N6 | 94.0(3) |
| Os1-N6 | 2.090(6) | N2-Os1-N3 | 97.9(2) |
| N5-C21 | 1.428(10) | N2-Os1-N4 | 99.0(3) |
| N5-C23 | 1.394(8) | N2-Os1-N6 | 167.9(2) |
| N6-C24 | 1.319(8) | N2-Os1-N5 | 91.4(2) |
| N6-C25 | 1.388(10) | N3-Os1-N4 | 78.8(3) |
| N7-C24 | 1.361(8) | N3-Os1-N6 | 93.2(2) |
| N7-C26 | 1.381(10) | N3-Os1-N5 | 169.3(2) |
| N8-C22 | 1.381(10) | N4-Os1-N6 | 87.8(2) |
| N8-C23 | 1.325(9) | N4-Os1-N5 | 94.6(3) |
| C21-C22 | 1.316(10) | N5-Os1-N6 | 78.0(3) |
| C23-C24 | 1.435(10) | | |
| C25-C26 | 1.349(9) | | |