Supporting Information

Synthesis and Reactivity of an Osmium(III) Aminoguanidine Complex

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Table of contents

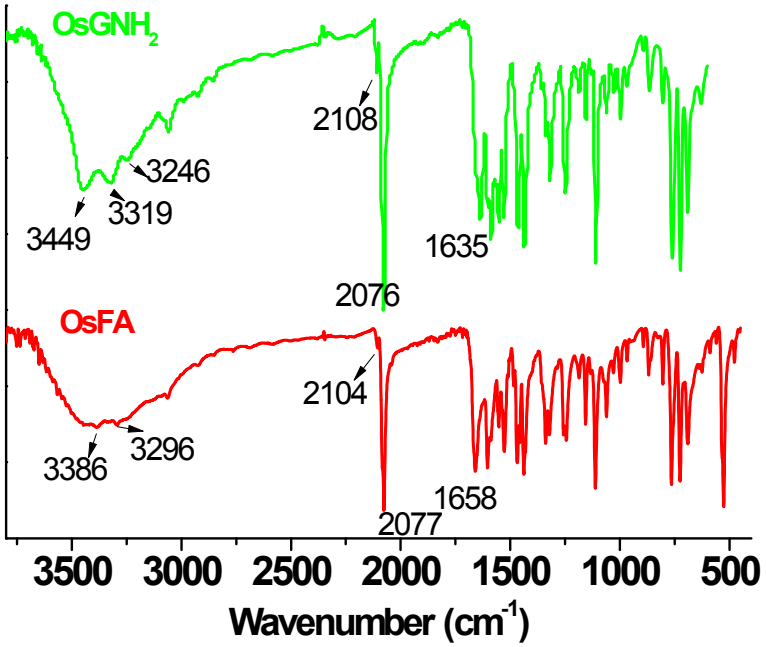

Figure S1. IR spectra of **$OsGNH_2$** and **OsFA**.

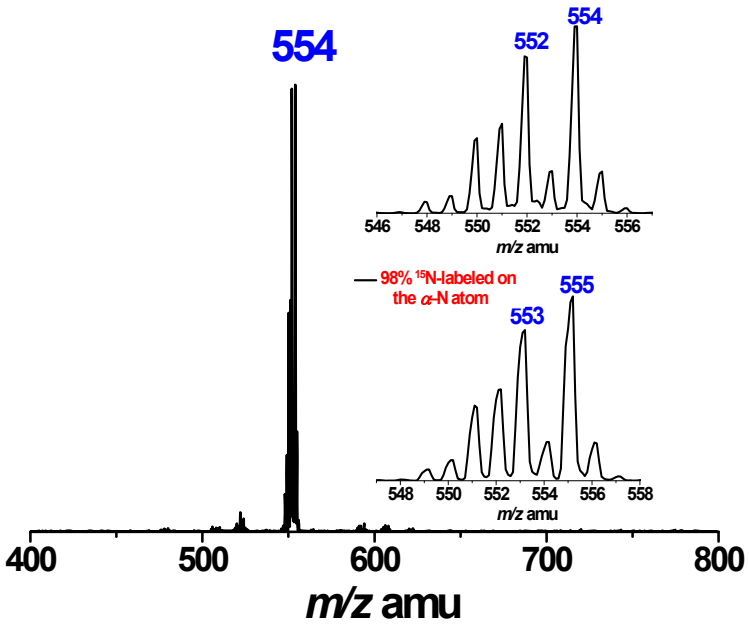

Figure S2. The ESI mass spectrum of $[Os\{N(H)C(NH_2)(NHNH_2\}(L)(CN)_3]^-$ (**$OsGNH_2$**) and experimental isotopic distribution patterns of the peaks at *m/z* = 554 and *m/z* = 555 (^{15}N labeled on the *α*-N atom).

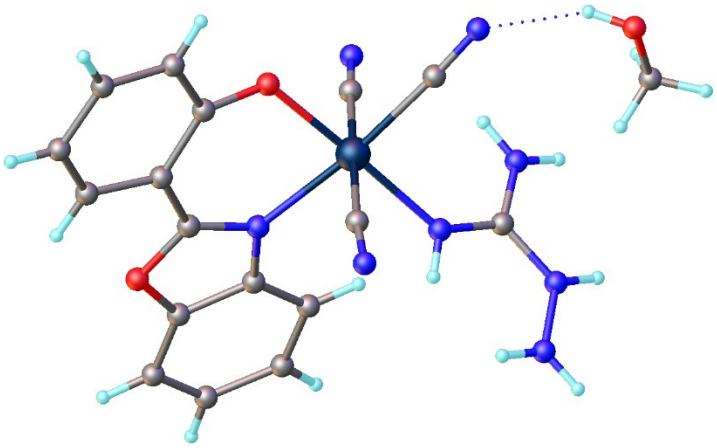

Figure S3. The H-bonding effects of a cyano group in **OsGNH$_2$** with MeOH.

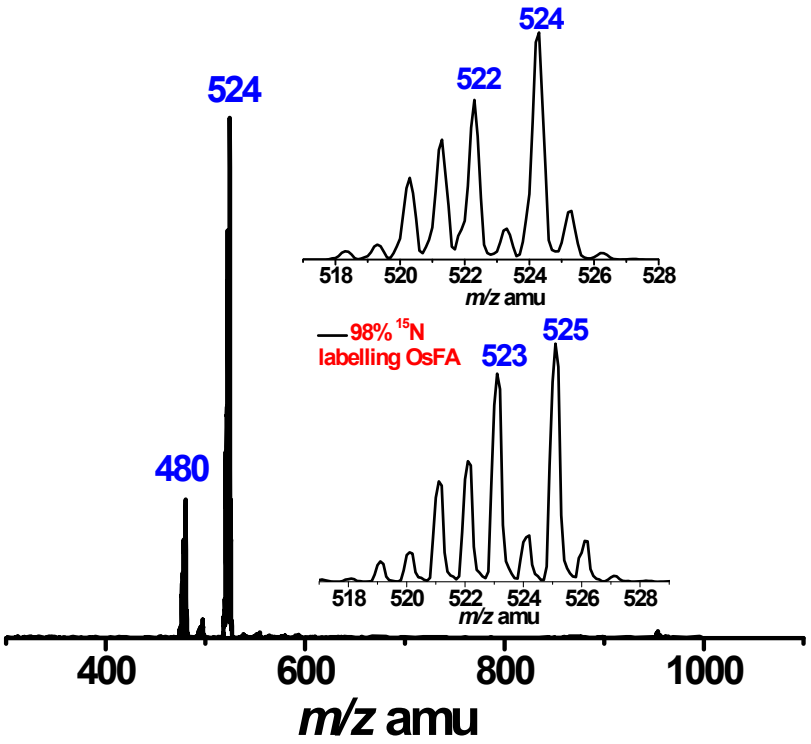

Figure S4. The ESI mass spectrum of $(PPh_4)[Os^{III}(\mathbf{L})(CN)_3(NH_2\text{-}CH{=}NH)]$ (**OsFA**) and experimental isotopic distribution patterns of the peaks at *m/z* = 524 and *m/z* = 525 (^{15}N labelling on the *α*-N atom).

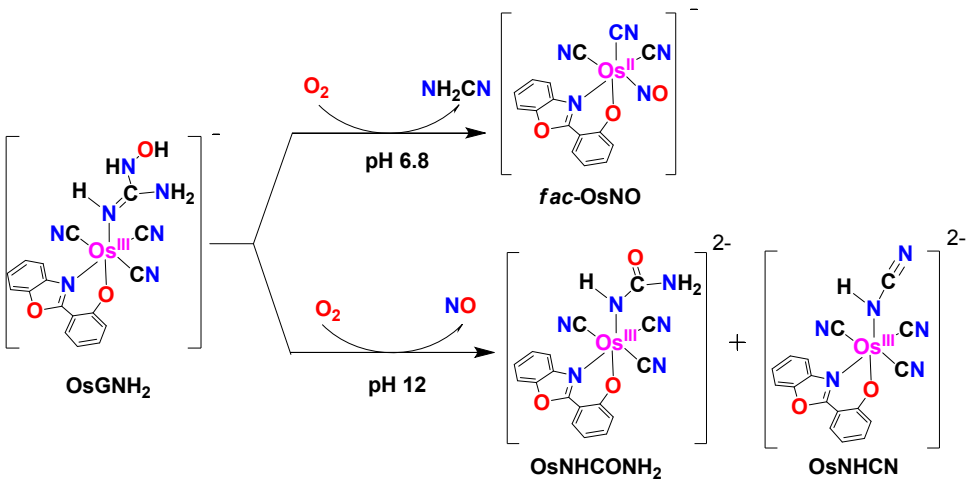

Figure S5. Aerobic oxidation of *γ*-**OsGOH** at different pH values.

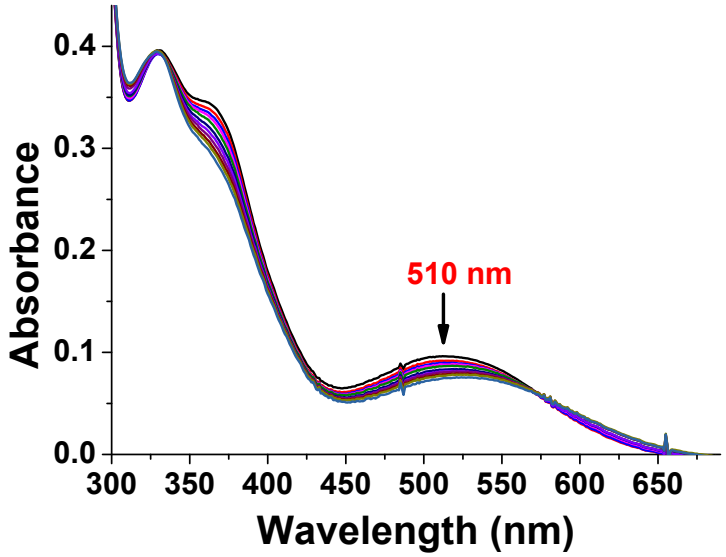

Figure S6. Spectral changes of the reaction of **$OsGNH_2$** (5×10^{-5} M) and H_2O_2 (2.5×10^{-3} M) in CH_3OH at 25 ˚C.

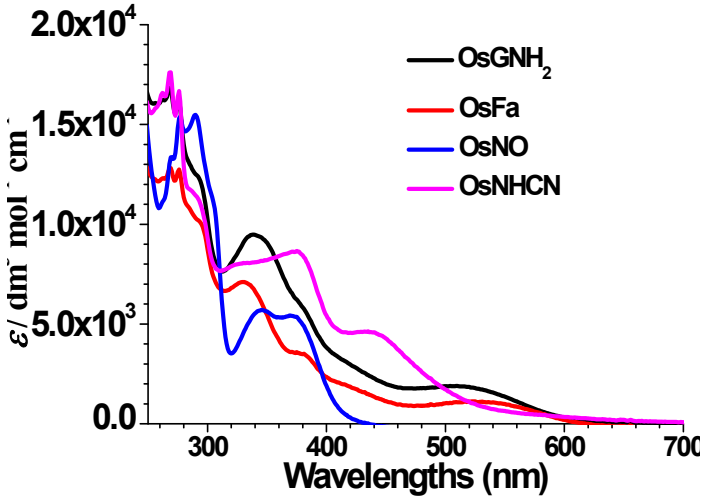

Figure S7. UV/vis absorption spectra of **OsGNH$_2$**, **OsFA**, *mer*-**OsNO** and **OsNHCN** in MeCN.

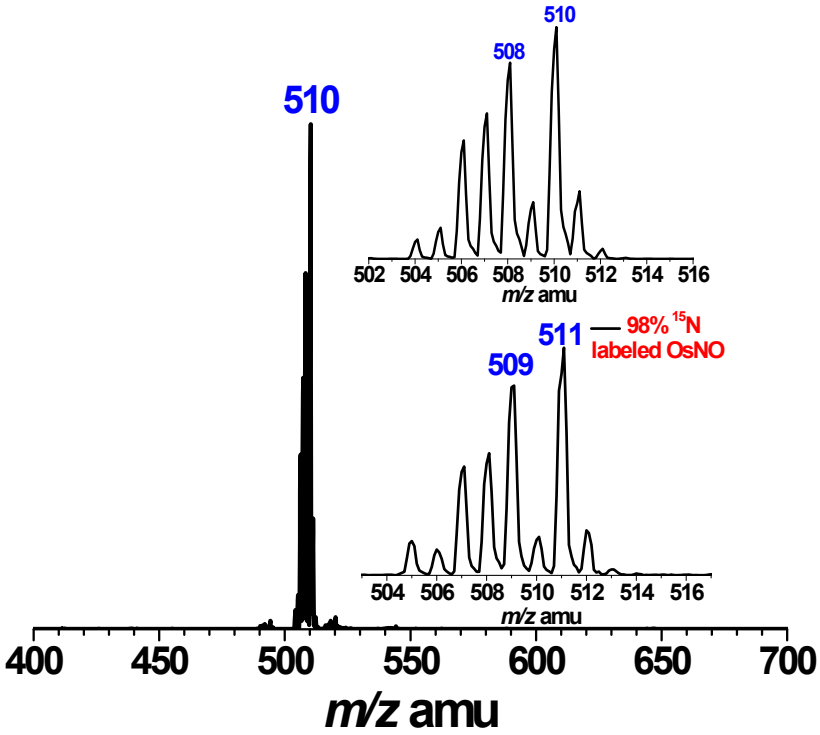

Figure S8. The ESI mass spectrum of $(PPh_4)[Os^{II}(NO)(\mathbf{L})(CN)_3]^-$ (***mer*-OsNO**) and experimental isotopic distribution patterns of the peaks at *m/z* = 510 and *m/z* = 511 (^{15}N labelling on the *α*-N atom).

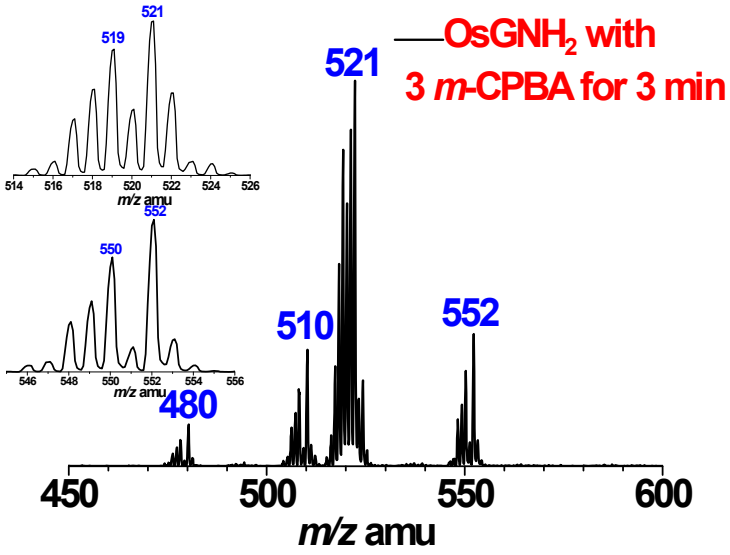

Figure S9. The ESI mass spectrum of ***mer*-OsGNH$_2$** with 3 equiv. of *m*-CPBA for 3 min and insert shows experimental isotopic distribution patterns of *m/z* = 552 and *m/z* = 521.

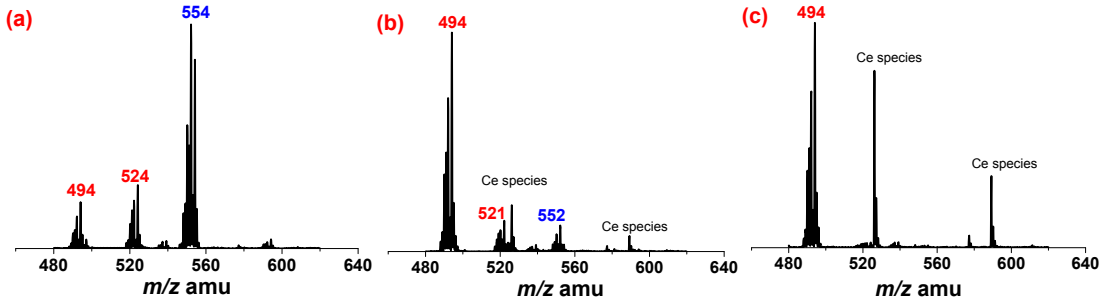

Figure S10. ESI/MS of **OsGNH$_2$** (0.1 mM) with 10 equiv. of Ce(IV). (a) 1 min; (b) 3 min; (c) 10 min.

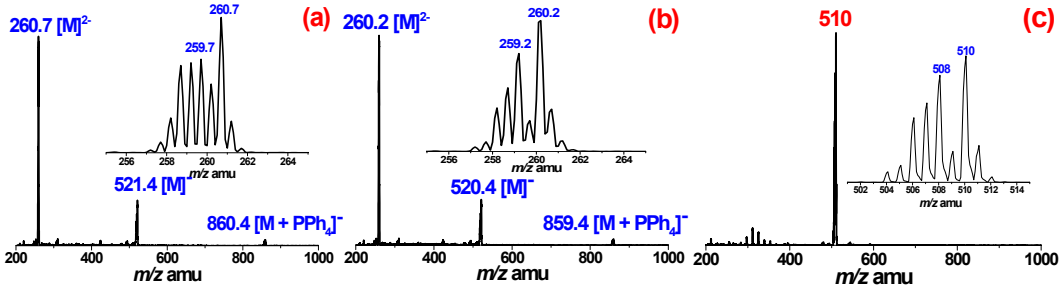

Figure S11. ESI/MS of **OsNHCN** (0.5 mM) with 10 equiv. of *m*-CPBA. (a) before mixing; (b) 5 min after mixing; (c) after 30 min.

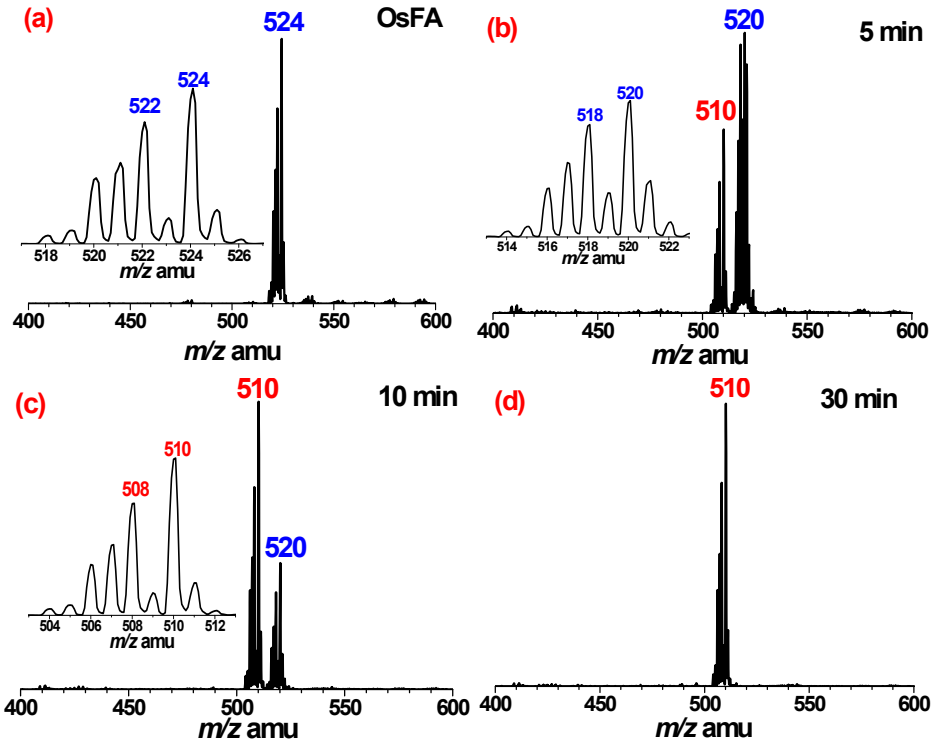

Figure S12. ESI/MS trace of **OsFA** (1.5 mM) with 10 equiv. of *m*-CPBA. (a) before mixing; (b) 5 min after mixing; (c) 10 min after mixing; (d) 30 min after mixing.

Table S1. Summary of crystal data, data collection and structure refinement for **$OsGNH_2$** and **OsFaA**.

Compound	**$OsGNH_2$**	**OsFA**
Formula	$PC_{41}H_{34}N_8O_2OsP{\cdot}CH_3OH$	$C_{41}H_{32}N_6O_2OsP$
Mr	923.97	861.90
T /K	153	153
Crystal syst	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a/Å	11.73820 (10)	11.76370 (10)
b/Å	16.3662 (2)	14.7379 (3)
c/Å	20.8351(2)	20.9329 (3)
α, (°)	/	/
β, (°)	/	/
γ, (°)	/	/
V/ Å^3	4002.62 (7)	3629.18 (10)
Z	4	4
ρ_{calcd}, Mg m^{-3}	1.533	1.577
Unique refl.	7164	5736
Final R indices,	0.027	0.044
I > 2σ(I), wR_2(all data)	0.071	0.115
GOF	1.03	1.04
No. of par.	499	461