Electronic Supplementary Information

The first crystallographically characterised ruthenium(VI) alkylimido porphyrin competent for aerobic epoxidation and hydrogen atom abstraction

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Table of contents

Abbreviations

2,6-Cl_2-TPP: 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato(2-)

2,6-F_2-TPP: 5,10,15,20-tetrakis(2,6-difluorophenyl)porphyrinato(2-)

TMP: 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrinato(2-)

4-Cl-TPP: 5,10,15,20-tetrakis(4-chlorophenyl)porphyrinato(2-)

F_{20}-TPP: 5,10,15,20-tetrakis(pentafluorophenyl)porphyrinato(2-)

TPP: 5,10,15,20-tetraphenylporphyrinato(2-)

3,4,5-$(MeO)_3$-TPP: 5,10,15,20-tetrakis(3,4,5-trimethoxyphenyl)porphyrinato(2-)

ACN: acetonitrile

AdN_3: 1-azidoadamantane

$AdNH_2$: 1-adamantylamine

PTFE: polytetrafluoroethylene

m-CPBA: *meta*-chloroperoxybenzoic acid

Experimental section

Material and instrumentation

Neutral alumina manufactured by Dieckmann Company was used for flash column chromatography. All chemicals were used as received and purchased from J&K Scientific and Tokyo Chemical Industry Co., LTD., except that *m*-CPBA and Zn dust were purchased from Sigma-Aldrich. The porphyrin ligands and $[Ru^{II}(Por)(CO)]$ (Por = TMP and 2,6-Cl_2-TPP) were synthesised according to the literature methods.[1,2] C_6D_6, $CDCl_3$ and CD_2Cl_2 were purchased from Cambridge Isotope Laboratories, Inc., and they were dried over 4 Å molecular sieves if necessary. ^1H and ^{19}F NMR spectra were recorded using a Bruker DPX300, DPX400, DPX500 or DPX600 spectrometer; the solvent $CDCl_3$ contains trimethylsilane (TMS) as an internal standard and all the chemical shifts were reported relative to TMS (for ^1H NMR). X-ray diffraction data of single crystals were collected on a Bruker APEX-II CCD diffractometer. Cyclic voltammetry was carried out on a Princeton Applied Research Model 273A potentiostat/galvanostat coulometer with a 3-electrode system (working electrode: glassy carbon; counter electrode: platinum wire; reference electrode: saturated calomel electrode). UV-vis spectra were recorded on a Cary 8454 UV-vis spectrophotometer (Agilent Technologies). If necessary, UV-vis sample could be injected into a UV-vis cell with side arm connectable to Schlenk line. Elemental analysis was performed by the Institute of Chemistry, the Chinese Academy of Sciences. GC-MS analysis was performed by Agilent Technologies 7890B GC system with 5977A MS detector (carrier gas: helium). High resolution ESI-MS experiment was carried out using Bruker's maXis II UHR-TOF mass spectrometer whereas

MALDI-TOF experiment was done using the "ultrafleXtreme^{TM}" (Bruker). Attenuated total-reflectance Fourier-transform infrared spectroscopy was conducted using the "Spectrum Two^{TM}" spectrometer (manufactured by PerkinElmer; Detector type: $LiTaO_3$).

Synthesis of [Ru^{III}(2,6-F_2-TPP)Cl(THF)] (1)

This complex was prepared by the reported method.[2]

Synthesis of [Ru^{II}(2,6-F_2-TPP)$(ACN)_2$] (2)

A Schlenk tube was charged with 10 mg of [Ru^{III}(2,6-F_2-TPP)Cl(THF)] and 70 equiv. of Zn dust (<10 μm). Deoxygenated and anhydrous solvents (fluorobenzene:ACN = 3.0:0.5 mL) were added to the tube equipped with a rubber septum via a PTFE-cannula. The reaction mixture was refluxed under argon overnight, and was then filtered with a PTFE filter to remove the fine Zn dust under argon. Removal of the solvents under high vacuum afforded the title compound. Yield: >99%.

Synthesis of [Ru^{VI}(2,6-F_2-TPP)$(NAd)_2$] (3)

Complex **2 (**12 mg) and AdN_3 (10 equiv.) were added to a Schlenk tube, followed by dissolving in 2 mL of deaerated and anhydrous benzene. This reaction mixture was stirred for extra 3 h to ensure completion of reaction. After cooling to RT and subsequent removal of solvent under vacuum, the reaction mixture was washed with a minimal amount of chilled *n*-pentane (anhydrous) under argon, so as to remove any unreacted AdN_3. Yield: 55%.

Synthesis of [Ru^{VI}(2,6-F_2-TPP)(NAd)(O)] (4)

Method A: In a typical procedure, 5 mg of **3** was dissolved in undried benzene, followed by slow vapour diffusion of *n*-pentane into this solution under argon at RT. The black block-like crystals obtained correspond to the title compound. Yield: 77%.

Method B: In a 50-mL round-bottom flask, 50 mg of [Ru^{II}(2,6-F_2-TPP)(CO)] was dissolved in CH_2Cl_2 (20 mL). After that, 70 mg of *m*-CPBA was added in a one-pot manner. Flash column chromatography (stationary phase: neutral alumina; eluent: CH_2Cl_2) was then used to purify [Ru^{VI}(2,6-F_2-TPP)$(O)_2$] (fast-moving brown band). The solution containing pure [Ru^{VI}(2,6-F_2-TPP)$(O)_2$] was concentrated to *ca*. 5 mL, followed by addition of $AdNH_2$ (100 mg) to generate [Ru^{VI}(2,6-F_2-TPP)$(NH_2Ad)_2$] (**5**). This reaction mixture was heated at 60 ^oC inside a seal tube for 1.5 h under 1 atm of O_2 atmosphere. After cooling down to RT, the reaction mixture was diluted with 5 mL of *n*-hexane and loaded into a neutral alumina column filled with *n*-hexane as mobile phase. 50 mL of a 1:1 (v/v) mixture of CH_2Cl_2/*n*-hexane was used to elute

impurities from the column. Subsequently, acetone/CH_2Cl_2 (1:4 v/v) was then added to elute [Ru^{VI}(2,6-F_2-TPP)(NAd)(O)]; the eluate was evaporated to dryness. If necessary, the sample can be further purified by washing with toluene/*n*-hexane (1:1 v/v) once/twice.

Synthesis of [Ru^{II}(2,6-F_2-TPP)($NH_2Ad)_2$] (5)

Complex **3** (5 mg) was dissolved in anhydrous *n*-hexane, followed by slow evaporation inside a glovebox. The brown crystals formed were the title compound. Yield: 50%.

Synthesis of [Ru^{VI}(2,6-Cl_2-TPP)(NAd)(O)] (6) and [Ru^{VI}(TMP)(NAd)(O)] (7)

[Ru^{II}(Por)($NH_2Ad)_2$] (Por = 2,6-Cl_2-TPP and TMP) were generated in situ by a procedure similar to that in Method B used for the synthesis of **4** through in-situ generation of **5**. The feasibility of using [Ru^{II}(Por)($NH_2Ad)_2$] as a precursor was exemplarily demonstrated by the use of **5 (**in isolated form) to react under aerobic and heating conditions. The purification of **7** requires recrystallisation using *n*-hexane after column chromatography while that of **6** is similar to the one used for the synthesis of **4**.

Synthesis of [Ru^{VI}(2,6-F_2-TPP)($O)_2$]

This complex was generated and purified as described in Method B used for the synthesis of **4**. Evaporation of the solution containing pure [Ru^{VI}(2,6-F_2-TPP)($O)_2$] to dryness afforded the title compound in isolated form.

X-ray crystal structure determination

Diffraction-quality crystals of **2** were grown by vapour diffusion of *n*-hexane into a benzene solution of **2** with a few drops of ACN. Single crystals of **4** were obtained by diffusing *n*-hexane into an undried benzene solution. For complex **5**, it was first dissolved in *n*-hexane containing a few drops of benzene, followed by slow evaporation in a well-circulated glovebox. The X-ray diffraction data were collected on a Bruker Proteum X8 diffractometer with monochromated Cu-*K*α radiation (the crystals were quickly mounted in a glass fiber and measured at a temperature of 100 K). The crystallographic data and structure refinement parameters are depicted in Table S1.

Table S1 Crystallographic data for **2**, **4**, and **5**

Complex	**2**	**4**	**5**
Chemical formula	$C_{48}H_{26}F_8N_6Ru \cdot 8.47(C_{2.12}H_{2.12})$	$C_{54}H_{35}F_8N_5ORu \cdot C_6H_6$	$C_{64}H_{54}F_8N_6Ru$
Crystal system, space group	Orthorhombic, *Pnnm*	Orthorhombic, $P2_12_12_1$	Monoclinic, C2/c
Temperature (K)	100	100	100
a, *b*, *c* (Å)	12.6211(4), 12.9645(4), 17.2046(5)	10.8463(2), 20.3999(4), 21.4989(4)	28.865(4), 12.4422(14), 18.7711(19)
β (°)	/	/	128.307(4)
V (Å^3)	2815.12(15)	4756.92(16)	5290.1(11)
Z	2	4	4
Radiation type	Cu-*K*α		
μ (mm^{-1})	2.88	3.37	3.05
Crystal size (mm)	0.3 × 0.07 × 0.05	0.25 × 0.06 × 0.05	0.1 × 0.06 × 0.06
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.598	0.600	0.562
No. of reflections	2609	8519	3814
No. of parameters	232	664	366
No. of restraints	25	0	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	0.90, −0.32	0.90, −0.53	0.89, −0.91
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$	0.061, 0.179	0.038, 0.103	0.053, 0.145
Goodness of fit, *S*	1.073	1.051	1.043

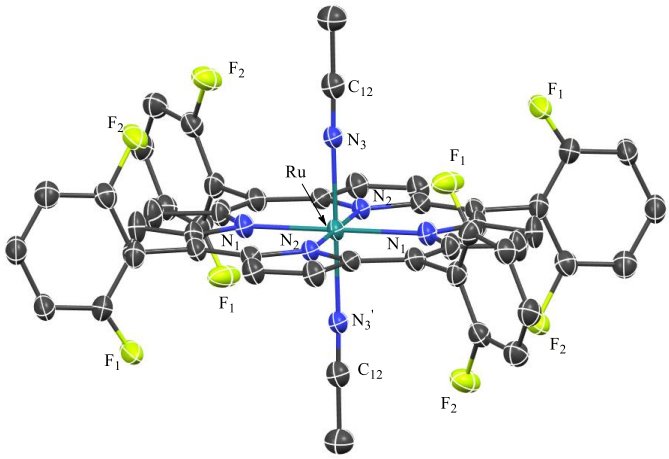


Fig. S1 ORTEP drawing of **2** (thermal ellipsoids drawn at 30% probability level). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ru–N_1 2.036(5), Ru–N_2 2.064(5), Ru–N_3 2.027(5), N_3–C_{12} 1.133(8); N_1-Ru-N_3: 89.4(2), N_1-Ru-N_3': 90.6(2), N_3-Ru-N_3': 180.0, Ru-N_3-C_{12}: 178.2(5).

Procedure for stoichiometric reaction of 3 or 4 with styrene/cyclohexa-1,4-diene/dihydroanthracene

In a sealable Schlenk tube, 5 μmol of **3** or **4** was dissolved in anhydrous benzene (CD_2Cl_2 was used for the reaction with cyclohexa-1,4-diene) under a positive flow of argon, followed by adding 100 equiv. of substrate (styrene, cyclohexa-1,4-diene or 9,-10-dihydroanthracene). Subsequently, the reaction mixture was degassed with three freeze-thaw cycles; the Schlenk tube containing the degassed reaction mixture was immersed into a pre-heated oil bath (temperature: 80 ^oC for styrene; RT for other substrates) overnight. Then, $PhSiMe_3$/chlorobenzene was added to the reaction mixture as internal standard for the determination of yield by ^1H NMR/GC, respectively. GC was used for the volatile substrates (styrene and cyclohexa-1,4-diene), whereas ^1H NMR was used for 9,10-dihydroanthracene. The yield of the oxidised product was defined as ([product]/[Ru]) ÷ n × (100/100), wherein [product] = concentration of product generated, [Ru] = concentration of Ru complex used initially, n = 1 for AdN=Ru=O complex **4** (assuming one mole of **4** produces, theoretically, 1 mole of oxidised product by undergoing a 2-electron reduction with Ru=O being the reactive group), n = 2 for AdN=Ru=NAd complex **3** (assuming one mole of **3** produces, theoretically, 2 moles of oxidised product by undergoing a 4-electron reduction).

Procedure of aerobic epoxidation catalysed by 4, 6 or 7

In a sealable Schlenk tube, 0.2 mmol of substrate and 0.002 mmol of catalyst (1 mol%)

were dissolved in 2 mL of CD_2Cl_2 or C_6D_6. The solution was then frozen by liquid nitrogen. A high vacuum was then applied to the frozen solution for several minutes. The tube was in turn sealed and allowed to thaw. An oxygen gas cylinder was purged for 30 to 60 s before connecting to the side arm of the seal tube. After that, oxygen gas was allowed to flow into the tube, which was then sealed immediately. The reaction mixture was stirred at RT for 24 h. Product turnover number was determined using $PhSiMe_3$ as an internal standard.

Computational details

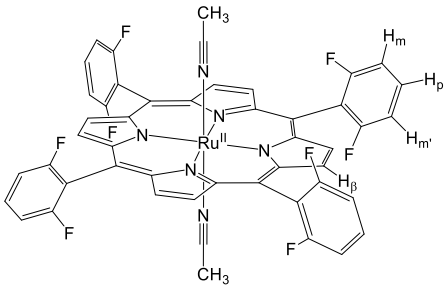
All calculations were performed using the G09 program package.[3] The real vibrational frequencies of optimised structures were computed to confirm that all the optimised structures are potential energy minima. For optimisation, we used the hybrid functional PBE0,[4] with dispersion corrections in revision three (D3)[5] due to its accuracy and wide applications to describing dispersion interactions.[6] The DFT-D3 method has been proved to provide reliable computed interaction energies as compared to the spin-component-scaled (SCS)-MP2 method for large complexes.[7] The valence atomic orbital of Ru was described by LANL2DZ basis set and the effective core potentials (ECPs) proposed by Hay and Wadt were employed.[8] The 6-31G* basis set[9] was used for hydrogen, carbon, oxygen, fluorine and nitrogen atoms. The initial geometry guess used for the optimization was directly obtained from its X-ray crystal structure.

To calculate the absorption spectra, TDDFT method with functional PBE0 has been used at the calculation level of PBE0-D3/LanL2DZ for Ru and 6-31g* for other atoms/PCM(CH_2Cl_2). First 30 excited states have been included in the simulated spectra. Gaussian functions have been adopted to simulate the absorption spectrum according to the equation:[10]

$$\varepsilon(\vartheta') = \frac{2.175.10^8 L.mol^{-1}cm^{-2}}{\Delta_{1/2}\vartheta'} f.\exp[-2.772(\frac{\vartheta' - \vartheta'_{i\to f}}{\Delta_{1/2}\vartheta'})^2]$$

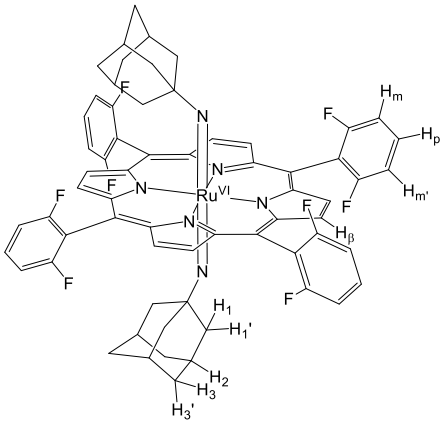
where the values of f and $\vartheta'_{i\to f}$ are derived from a quantum mechanical calculation. $\Delta_{1/2}\vartheta'$, which is the full-width half-maximum (FWHM) of the band, was set as 2000 cm^{-1} when convoluting the spectra.

Characterisation of ruthenium porphyrins 2–7 and [Ru^{VI}(2,6-F_2-TPP)$(O)_2$]



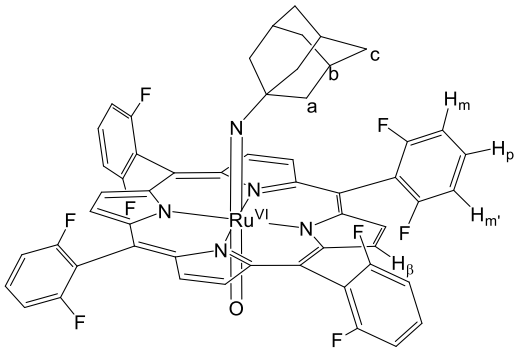
[Ru^{II}(2,6-F_2-TPP)$(ACN)_2$] (2)

^{1}H NMR (C_6D_6, 300 MHz): δ 8.56 ($H_{β,}$ s, 8H), 7.09 (H_p, m, 4H), 6.96 (H_m & $H_{m'}$, m, 8H), –2.07 (*CH*$_3$CN, s, 6H); HRMS (ESI$^+$): *m*/*z* 940.1160 (M^+, calcd: 940.1135); ATR-FTIR: oxidation state marker band: < 1014 cm^{-1} (obscured by the strong ligand signal at 1000 cm^{-1}). Attempts to obtain other characterisation data for **2** have not been successful due to its high sensitivity towards oxygen.



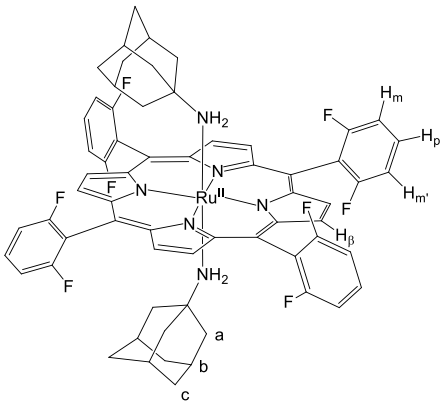
[Ru^{VI}(2,6-F_2-TPP)$(NAd)_2$] (3)

^{1}H NMR (C_6D_6, 400 MHz): δ 8.70 ($H_{β,}$ s, 8H), 7.09 (H_p, m, 4H), 6.99 (H_m & $H_{m'}$, m, 8H), 0.29–0.50 ($H_{1'}$, H_2, H_3 & $H_{3'}$, m, 24H), –2.16 (H_1, s, 6H); ^{19}F NMR (C_6D_6, 376 MHz): δ –108.1; UV-vis (CH_2Cl_2): $λ_{max}$ (log ε) 406 (5.10), 417 (5.20), 462 (4.18), 507 (4.38), 535 (sh, 4.16), 585 nm (3.94); HRMS (ESI$^+$): readily decomposed in ESI-MS capillary tubing (with moisture); MALDI-TOF (dipping one drop of sample followed by immediate drying): 1007.1760 ([M – NAd]$^+$, calcd: 1007.1817). Attempts to obtain other characterisation data for **3** have not been successful due to its high sensitivity towards moisture, similar to an analogue reported.[11]



[Ru^{VI}(2,6-F_2-TPP)(NAd)(O)] (4)

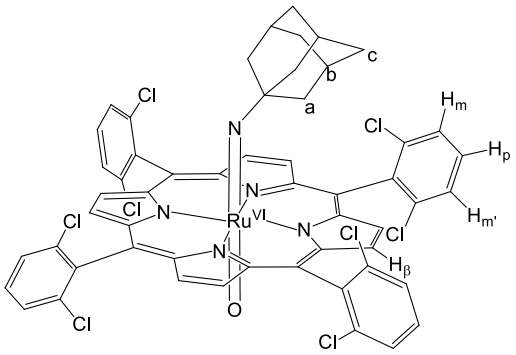
^{1}H NMR (C_6D_6, 400 MHz): δ 8.91 ($H_{β,}$ s, 8H), 7.06–7.04 (H_p, m, 4H), 6.86–6.90 (H_m & $H_{m'}$, m, 8H), 0.18–0.15 ($H_{c'}$ & H_b, d + s, 6H), –0.12 (H_c, d, 3H), –2.16 (H_a, s, 6H); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.93 ($H_β$, s, 8H), 7.79–7.83 (H_p, m, 4H), 7.45–7.50 ($H_{m'}$, m, 4H), 7.30–7.35 (H_m, m, 4H), 0.36–0.41 ($H_{c'}$ & H_b, d + s, 6H), –0.08 to –0.01 (H_c, d, 3H), –2.53 (H_a, s, 6H); ^{13}C NMR without ^{19}F decoupling ($CDCl_3$, 150 MHz): δ 163.01–163.63 (d), 161.35–161.99 (d), 142.41, 130.88 (t), 129.03, 128.23, 125.29, 118.86–119.13 (t), 111.53–111.70 (d), 110.89–110.06 (d), 107.81, 57.75, 35.24, 33.89, 26.00; ^{19}F NMR (C_6D_6, 376 MHz): δ –105.8, –108.7; UV-vis (CH_2Cl_2): $λ_{max}$ (log ε) 411 (5.18), 553 nm (4.46); HRMS (ESI^+): 1024.1783 ($[M + H]^+$, calcd: 1024.1845); ATR-FTIR: oxidation state marker band: 1014 cm^{-1}; Anal. Calcd for $C_{54}H_{35}F_8N_5ORu$: C 63.40, H 3.45, N 6.85; found: C 63.61, H 3.63, N 6.74.



[Ru^{II}(2,6-F_2-TPP)($AdNH_2$)$_2$] (5)

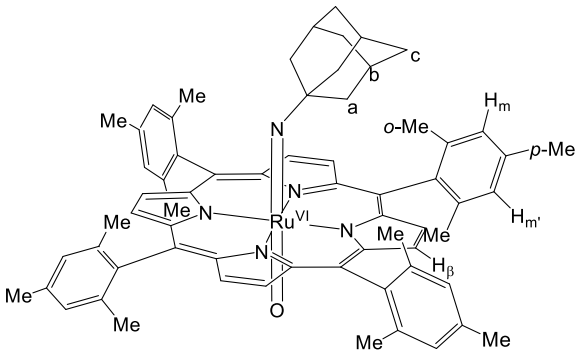
^{1}H NMR (C_6D_6, 400 MHz): δ 8.34 ($H_{β,}$ s, 8H), 6.98–7.00 (H_p, m, 4H), 6.90–6.96 (H_m & $H_{m'}$, m, 8H), 0.67–0.69 (H_c, m, 6H), 0.34–0.38 (H_b & $H_{c'}$, d, 12H), –1.78 (H_a+ $H_{a'}$+NH_2, s, 16H); ^{13}C NMR without ^{19}F decoupling ($CDCl_3$, 150 MHz): δ 161.68–163.36 (d), 144.62, 132.13, 129.66–129.79 (t), 127.67, 127.52, 119.00–119.29 (t), 110.08–110.91 (d), 108.73, 46.62, 39.73, 34.82, 28.03; ^{19}F NMR (C_6D_6, 376 MHz): δ –112.0; HRMS (ESI^+): 1160.3211 (M^+, calcd: 1160.3326); UV-vis (CH_2Cl_2): $λ_{max}$ (log ε) 406 (5.10), 503 (4.34); ATR-FTIR: oxidation state marker band: < 1014 cm^{-1}

(obscured by the strong ligand signal at 1000 cm^{-1}); Anal. Calcd for $C_{64}H_{54}F_8N_6Ru$: C 66.25, H 4.69, N 7.24; found: C 66.41, H 4.81, N 7.24.



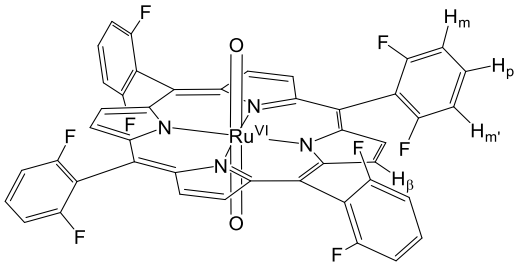
[Ru^{VI}(2,6-Cl_2-TPP)(NAd)(O)] (6)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.71 ($H_β$, s, 8H), 7.83–7.85 (H_p, m, 4H), 7.77–7.80 ($H_{m'}$, m, 4H), 7.69–7.72 (H_m, m, 4H), 0.39–0.44 ($H_{c'}$ & H_b, d + s, 6H), –0.11 to –0.09 (H_c, d, 3H), –2.19 (H_a, s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 141.71, 139.68, 139.42, 138.35, 130.49, 130.25, 129.54, 129.04, 128.14, 127.57, 115.93, 57.85, 35.79, 34.14, 26.07; HRMS (ESI^+): 1155.9487 ($[M + H]^+$, calcd: 1155.9430); ATR-FTIR: oxidation state marker band: 1014 cm^{-1}; UV-vis (CH_2Cl_2): $λ_{max}$ (log ε) 418 (5.10), 557 nm (4.28); Anal. Calcd for $C_{54}H_{35}Cl_8N_5ORu$: C 56.17, H 3.06, N 6.07; found: C 56.32, H 3.34, N 6.42.



[Ru^{VI}(TMP)(NAd)(O)] (7)

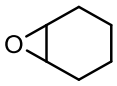
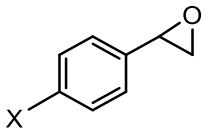
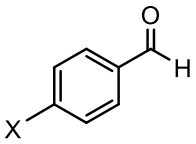
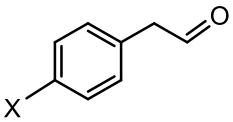
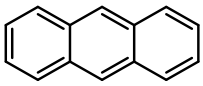
^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.67 ($H_β$, s, 8H), 7.25–7.28 (H_m & $H_{m'}$, m, 8H), 2.74 (*p*-Me, s, 12H), 2.00 (*o*-Me, s, 12H), 1.87 (*o'*-Me, s, 12H), 0.43–0.46 ($H_{c'}$ & H_b, d + s, 6H), –0.08 to 0.05 (H_c, m, 3H), –2.26 (H_a, s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 141.68, 140.42, 138.64, 138.60, 137.50, 129.92, 127.91, 127.47, 123.86, 123.19, 119.09, 57.61, 36.35, 34.05, 26.07, 22.51, 22.07, 21.49; HRMS (ESI^+): 1048.4502 ($[M + H]^+$, calcd: 1048.4467); ATR-FTIR: oxidation state marker band: 1014 cm^{-1}; UV-vis (CH_2Cl_2): $λ_{max}$ (log ε) 418 (5.16), 531 nm (4.20); Anal. Calcd for $C_{66}H_{67}N_5ORu$: C 75.69, H 6.45, N 6.69; found: C 75.95, H 6.98, N 6.90.



[Ru^{VI}(2,6-F_2-TPP)$(O)_2$]

^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.12 ($H_{β,}$ s, 8H), 7.85–7.88 (H_p, m, 4H), 7.43–7.46 (H_m & $H_{m'}$, m, 8H); ATR-FTIR: oxidation state marker band: 1018 cm^{-1}; UV-vis (CH_2Cl_2): $λ_{max}$ (log ε) 414 (5.20), 511 nm (4.41).

Table S2 References for the known organic compounds

Structure of the known organic compound	Reference
	Ref. 12
	Ref. 13
	X = NO_2: Ref. 14 X = ^{t}Bu: Ref. 15 X = H: Ref. 16
	X = ^{t}Bu: Ref. 17 X = H: Ref. 18
	X = ^{t}Bu: Ref. 19 X = H: Ref. 20
	Ref. 21

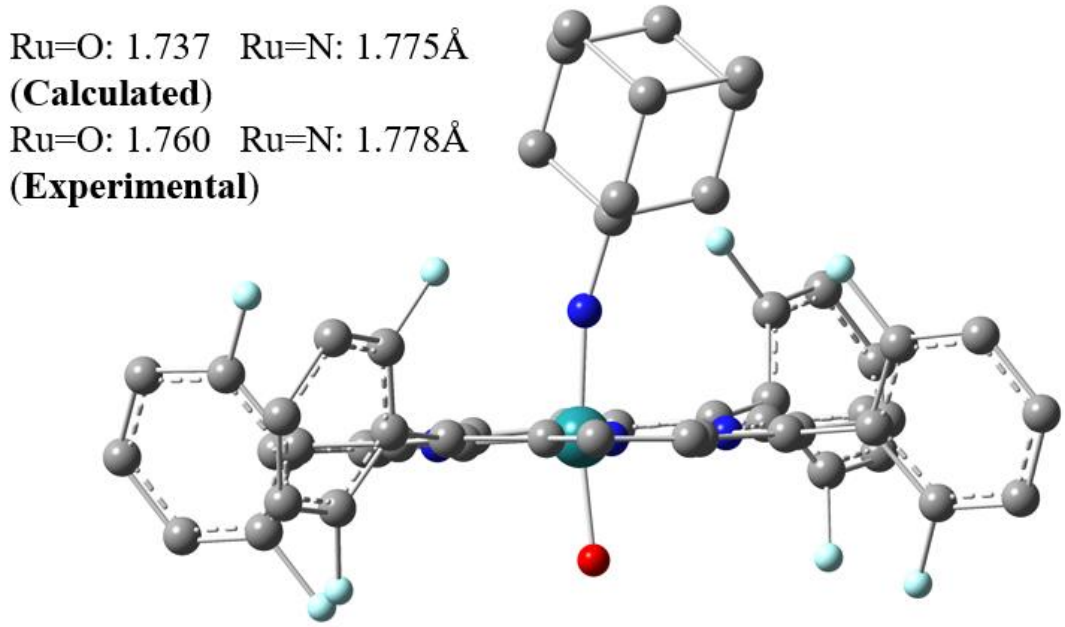


Fig. S2 DFT-optimised structure of **4** used for calibration.

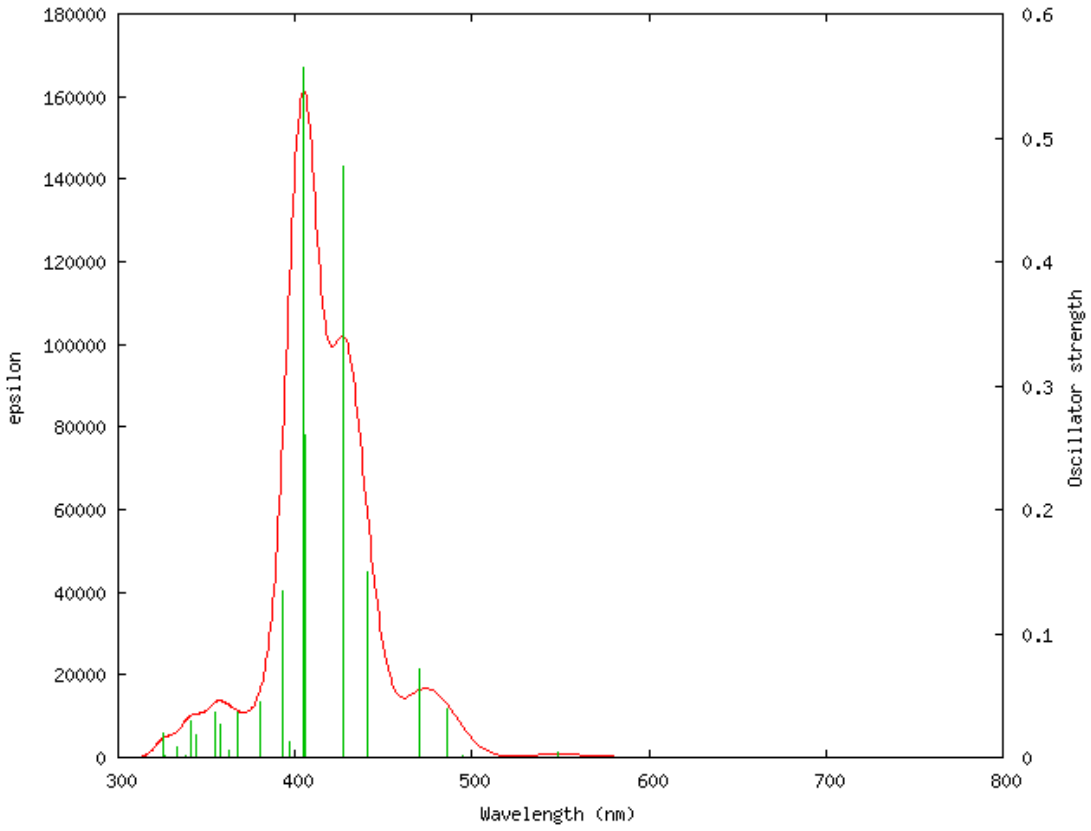


Fig. S3 TDDFT-simulated UV-vis spectrum of **3** (angle of Ru=N-C(Ad) bond: 140^{o}).

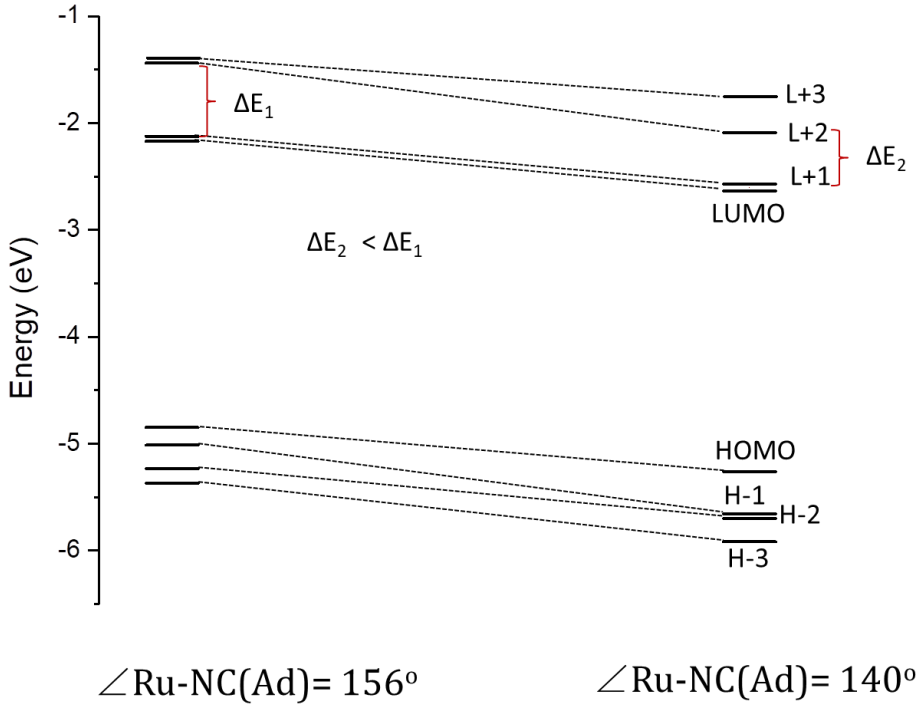


Fig. S4 DFT-calculated MO diagram of **3** showing the angle relationship. It shows that the Soret band of the porphyrin ligand will partly mix with the transition from π to π*(Ru-NC(Ad)) when dihedral angle decreases (as ΔE becomes smaller), resulting in two close-lying transitions with comparable peak intensities.

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Coordinates of DFT-optimised structures

3

Ru	0.34203800	0.00181800	0.01433000
F	0.90486300	-5.00023600	2.23983900
F	-0.18037000	-4.96040600	-2.31895900
F	5.33723100	0.84304700	2.22342500
F	5.35982800	-0.74880000	-2.18686400
F	-0.24443300	5.06318700	2.24007200
F	0.79543700	4.90067200	-2.32629700
F	-4.68754800	0.76766300	2.23002600
F	-4.68677300	-0.84928600	-2.17649000
N	1.81978600	-1.44544100	-0.01001400
N	1.79412900	1.47457700	0.03233200
N	-1.15354400	1.44635800	0.04398700
N	-1.12817200	-1.46875100	-0.01301100
N	0.25213200	0.04102000	-1.77538800
C	1.60895600	-2.78717600	-0.01912900
C	2.88782600	-3.46056800	-0.01192300
H	3.02739000	-4.53298700	-0.02193800
C	3.84283500	-2.49602200	0.00981900
H	4.91593100	-2.62757700	0.03225000
C	3.15846700	-1.22209700	0.00558600
C	3.78612500	0.03184900	0.01654900
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C	8.08714600	0.07403400	0.02259500
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C	7.40397200	-0.34524300	-1.11509500
H	7.92082300	-0.66217000	-2.01429600
C	6.01692100	-0.34883000	-1.09374000
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H	2.94646700	4.58281200	-0.00729200

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H	0.21761400	8.80728500	-0.19246200
C	-0.02349200	7.07716900	1.05600200
H	-0.24382200	7.62385500	1.96635000
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H	-1.10425400	1.09871100	6.77937600

4

Ru	-0.27061100	0.00069200	-0.73136900
F	-1.47195800	-5.18154200	-2.60196500
F	0.52467500	-4.78807700	1.62356200
F	-5.42746400	1.05520900	-2.46079600
F	-5.04855300	-0.53239600	1.93387000
F	0.37734400	5.31542400	-2.66302000
F	-0.29729100	4.61259400	1.92146400
F	4.59685700	0.47017000	-3.48587600
F	4.83848100	-0.94953100	0.97769300
O	-0.31737600	0.00089400	-2.46820200
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N	1.27556200	1.39543600	-0.92096900
N	1.12820400	-1.53825100	-0.90805900
N	0.06562600	-0.00165600	1.01116300
C	-1.62927300	-2.73540600	-0.55997000
C	-2.92769500	-3.34729600	-0.41321500
H	-3.11141000	-4.41071700	-0.34934100

C	-3.84197400	-2.34372300	-0.38029800
H	-4.91630500	-2.43008500	-0.29512200
C	-3.11404000	-1.10234500	-0.48185700
C	-3.68736600	0.17494700	-0.42884900
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C	-5.99221600	0.69538700	-1.30575800
C	-7.37154200	0.78114300	-1.18230100
H	-7.95757600	1.13094300	-2.02506900
C	-7.95803100	0.40771000	0.02305200
H	-9.03621500	0.46678100	0.13721400
C	-7.17654700	-0.04017400	1.08407200
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C	-5.80149800	-0.10556700	0.91438900
C	-2.98721500	1.38828300	-0.47389800
C	-3.58236800	2.69573200	-0.33988900
H	-4.63978100	2.88880800	-0.22332500
C	-2.56954000	3.60063200	-0.37331800
H	-2.63871400	4.67767500	-0.30448200
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H	0.26266100	8.73601200	0.23870600
C	0.33317800	7.16882100	-1.22703600
H	0.50151300	7.81794100	-2.07933900
C	0.24482900	5.79804500	-1.42553200
C	1.13862400	2.73957800	-0.79791900
C	2.44442200	3.35031600	-0.87155000
H	2.64118200	4.41121600	-0.80032800
C	3.34298000	2.34511400	-1.04093500
H	4.41748100	2.42539100	-1.13258000
C	2.59576700	1.10906100	-1.06370200
C	3.16140000	-0.17089000	-1.14657300
C	4.64146000	-0.24354500	-1.25466600
C	5.31705300	0.08436900	-2.43111800

C	6.69878900	0.02991500	-2.54779300
H	7.16096200	0.29463700	-3.49247200
C	7.44708700	-0.36862900	-1.44444700
H	8.52922600	-0.41782300	-1.51842200
C	6.82296800	-0.70363100	-0.24606200
H	7.38288100	-1.01231500	0.62988300
C	5.44016700	-0.63176900	-0.17869800
C	2.46723000	-1.38636800	-1.08314000
C	3.07711800	-2.69426200	-1.14052300
H	4.13066700	-2.88350200	-1.29418100
C	2.08180700	-3.60488800	-0.98096200
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C	0.85136000	-2.86361600	-0.83277100
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C	0.01263800	-5.54523100	0.64482700
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H	0.37648900	-7.35009900	1.73194300
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H	-1.46416400	-7.71463800	-2.17048500
C	-0.99448200	-5.74359700	-1.48877000
C	0.71906100	-0.00253300	2.24730000
C	1.60519200	1.25909700	2.39915500
H	0.98566100	2.15414600	2.26207600
H	2.36445000	1.25575000	1.60886900
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C	-0.36057700	-0.00005500	3.35958200
H	-0.99685400	-0.88464700	3.23396900
H	-0.99494500	0.88569900	3.23217100
C	0.31706700	0.00090600	4.73322100
H	-0.45894700	0.00241000	5.51011000
C	1.60443200	-1.26405700	2.40110400
H	2.36569100	-1.26407200	1.61427900
H	0.98631800	-2.15979200	2.26443800
C	2.26606800	-1.25376100	3.78357200

H	2.88954400	-2.15250000	3.87801600
C	3.14068900	-0.00143300	3.92222900
H	3.92182100	-0.00581100	3.15143100
H	3.64248600	-0.00049000	4.89977600
C	1.18969800	1.25392000	4.87120100
H	1.65968000	1.27650200	5.86409800
H	0.56882700	2.15628500	4.78480100
C	1.18877000	-1.25244700	4.87434400
H	0.56701400	-2.15444300	4.79100900
H	1.65880100	-1.27261100	5.86731000

3 (bond angle of Ru=N-C bond was fixed at 140^{o})

Ru	-0.52931415	-0.00118754	0.01517311
F	-1.07210785	4.99544814	2.25776491
F	0.00511375	4.96683011	-2.30301729
F	-5.52337935	-0.83340626	2.23022384
F	-5.54844489	0.77273435	-2.17486685
F	0.04462302	-5.07158331	2.22357058
F	-1.00260268	-4.89097060	-2.34043723
F	4.50158830	-0.79042119	2.21964541
F	4.49843232	0.84073850	-2.18162933
N	-2.00241211	1.45090772	-0.00193864
N	-1.98612917	-1.46929962	0.03095257
N	0.96163566	-1.45063858	0.03757560
N	0.94559653	1.46470619	-0.00998383
N	-0.44262732	-0.03490202	-1.77481561
C	-1.78725838	2.79197735	-0.00709617
C	-3.06392883	3.46946946	0.00450240
H	-3.20003963	4.54236043	-0.00181405
C	-4.02201448	2.50794763	0.02479569
H	-5.09463898	2.64289461	0.04951544
C	-3.34177983	1.23183918	0.01526804
C	-3.97347158	-0.02010209	0.02328089
C	-5.45860879	-0.02903677	0.02774864
C	-6.19232512	-0.44011169	1.14188968
C	-7.57912818	-0.45993092	1.16972459
H	-8.08634870	-0.78873801	2.07013847

C	-8.27459002	-0.04841525	0.03666575
H	-9.36038325	-0.05580962	0.04011961
C	-7.59202942	0.37232362	-1.10085287
H	-8.10940501	0.69381936	-1.99812835
C	-6.20493917	0.37136191	-1.08189704
C	-3.32783716	-1.26504472	0.02258468
C	-3.99397210	-2.54837885	-0.00137854
H	-5.06522119	-2.69468504	-0.02110339
C	-3.02500123	-3.49924827	-0.00524401
H	-3.14858394	-4.57365286	-0.01668495
C	-1.75603947	-2.80768345	0.01120745
C	-0.50195316	-3.42947803	0.00026669
C	-0.48768256	-4.91370766	-0.05376865
C	-0.74021326	-5.60350181	-1.23918720
C	-0.72891546	-6.98804699	-1.32356482
H	-0.93278872	-7.46468471	-2.27612974
C	-0.44821384	-7.72153095	-0.17412874
H	-0.43373628	-8.80629769	-0.22020985
C	-0.18487777	-7.08100856	1.03340225
H	0.03525472	-7.63133925	1.94159957
C	-0.21033812	-5.69419560	1.06784231
C	0.74616276	-2.79052562	0.01339530
C	2.02035937	-3.46769625	-0.02286413
H	2.15495941	-4.54005883	-0.05766764
C	2.98149432	-2.50719136	-0.01924280
H	4.05370464	-2.64352778	-0.05241939
C	2.30376472	-1.23304444	0.01926538
C	2.93564325	0.01822420	0.01870609
C	4.42000226	0.02582143	0.01949840
C	5.16292628	-0.38123069	1.12864649
C	6.54919193	-0.38463437	1.15524091
H	7.06182620	-0.71130245	2.05332889
C	7.23758671	0.03899719	0.02220757
H	8.32328475	0.04421731	0.02326689
C	6.54736865	0.45583641	-1.11223515
H	7.05866839	0.78698600	-2.00944349
C	5.16111544	0.43915699	-1.08860408
C	2.29011844	1.26240172	0.01311960

C	2.95342302	2.54443340	0.03757750
H	4.02389642	2.69314806	0.07314957
C	1.98164446	3.49402104	0.02215256
H	2.10388017	4.56829208	0.04132544
C	0.71508107	2.80208783	-0.00837433
C	-0.53997495	3.42765816	-0.01405882
C	-0.54081230	4.91288140	-0.02334691
C	-0.26412863	5.64136391	-1.17988306
C	-0.25465427	7.02823911	-1.21318061
H	-0.03438732	7.53609110	-2.14575802
C	-0.53430430	7.72376217	-0.04019831
H	-0.53275432	8.80957657	-0.04702585
C	-0.81473623	7.04379359	1.14170211
H	-1.03088948	7.56380660	2.06852548
C	-0.80948809	5.65659020	1.12520482
C	0.51114281	-0.06722465	-2.80547827
C	1.37288258	-1.35300433	-2.75522075
H	0.71063094	-2.22850888	-2.75987689
H	1.93506875	-1.36946992	-1.81542263
C	2.33621361	-1.38445252	-3.94703620
H	2.93910443	-2.30095407	-3.88967723
C	-0.27215862	-0.05531980	-4.14462776
H	-0.89427153	0.84788788	-4.17626907
H	-0.94731185	-0.92005615	-4.16098242
C	0.69707698	-0.09431718	-5.33029935
H	0.11838216	-0.08495569	-6.26383188
C	1.44924205	1.16365603	-2.77339309
H	2.01715588	1.15785863	-1.83808625
H	0.84250389	2.07822957	-2.78652111
C	2.40984174	1.11955921	-3.96736617
H	3.06661987	1.99878640	-3.92353074
C	3.25543619	-0.15807781	-3.89266962
H	3.83924825	-0.16447538	-2.96331829
H	3.96879100	-0.18632229	-4.72854419
C	1.54144164	-1.37205740	-5.25693407
H	2.22708187	-1.42032687	-6.11457157
H	0.89100221	-2.25606457	-5.31059337
C	1.61543144	1.13223905	-5.27747424

H	1.01838403	2.05210902	-5.34627494
H	2.30240096	1.12596567	-6.13547021
N	-0.44271227	0.03265405	1.80523889
C	0.51094942	0.06904551	2.83588330
C	1.37262981	1.35453266	2.78062116
H	0.70962090	2.22946816	2.78140807
H	1.93476163	1.36742765	1.84080011
C	2.33540204	1.39149482	3.97272523
H	2.93823606	2.30778383	3.91158499
C	-0.27260809	0.06276092	4.17495676
H	-0.89478532	-0.84027517	4.21040293
H	-0.94796231	0.92742113	4.18733104
C	0.69617951	0.10696340	5.36083684
H	0.11708319	0.10134164	6.29414803
C	1.44922530	-1.16186961	2.80929934
H	2.01709264	-1.16081578	1.87387610
H	0.84190433	-2.07601209	2.82685146
C	2.40947995	-1.11249228	4.00346845
H	3.06652801	-1.99171124	3.96375143
C	3.25483854	0.16506587	3.92412545
H	3.83976345	0.16823159	2.99557964
H	3.96727728	0.19684339	4.76066244
C	1.54029325	1.38460869	5.28238738
H	2.22570082	1.43659457	6.13997149
H	0.88965743	2.26868087	5.33227196
C	1.61473513	-1.11969437	5.31341219
H	1.01779533	-2.03932744	5.38612458
H	2.30155007	-1.10967825	6.17147924

[Ru^{VI}(2,6-F_2-TPP)$(O)_2$]

Ru	0.03459073	-0.00023390	0.00036354
F	0.89474242	4.95238784	-2.26792563
F	-0.86110315	5.06108666	2.07707997
F	5.01744489	-0.82195144	-2.19859283
F	5.02197623	0.79701185	2.20002213
F	-0.88653858	-5.05465610	-2.07889981
F	0.86971657	-4.95922375	2.26624655
F	-5.00365929	-0.92925800	-2.14571585

F	-4.99795952	0.95450188	2.14723088
O	-0.18858395	-0.00545264	-1.71121952
N	1.47125669	1.44897251	-0.01071690
N	1.46382439	-1.45639845	0.01181600
N	-1.46615330	-1.47069364	0.00953736
N	-1.45871889	1.47796719	-0.00921245
C	1.25039610	2.79974136	-0.02194498
C	2.52359497	3.46831077	-0.00831232
H	2.66054763	4.54052125	0.00022278
C	3.48671238	2.50907117	-0.00378838
H	4.55861752	2.64859193	-0.00612787
C	2.81996228	1.23584531	-0.00181931
C	3.45955183	-0.00876476	0.00090225
C	4.94466873	-0.01252192	0.00080382
C	5.68263815	-0.42196964	-1.11135848
C	7.06942333	-0.43573248	-1.13436711
H	7.58101761	-0.76367738	-2.03255976
C	7.75913867	-0.01938747	0.00043181
H	8.84490614	-0.02205505	0.00030745
C	7.07175436	0.40042049	1.13536884
H	7.58517959	0.72596504	2.03338792
C	5.68491732	0.39346234	1.11272217
C	2.81363702	-1.25009658	0.00340737
C	3.47387242	-2.52670653	0.00533252
H	4.54504465	-2.67178788	0.00811282
C	2.50592945	-3.48107770	0.00910873
H	2.63739348	-4.55396446	0.00032333
C	1.23614641	-2.80610577	0.02247733
C	-0.00752067	-3.44627001	0.05601976
C	-0.00753443	-4.93118688	0.09139632
C	0.43128634	-5.64605666	1.20764916
C	0.43527210	-7.03195864	1.26338793
H	0.78711412	-7.52469198	2.16307445
C	-0.02157085	-7.74497683	0.15897966
H	-0.02686157	-8.83043208	0.18498237
C	-0.47179168	-7.08125785	-0.97832861
H	-0.82916730	-7.61305982	-1.85324646
C	-0.45471090	-5.69434461	-0.98907514

C	-1.25697642	-2.80916336	0.06347534
C	-2.53361335	-3.47704484	0.14199836
H	-2.67443483	-4.54656075	0.21301342
C	-3.48719869	-2.51092964	0.12855832
H	-4.55910754	-2.63868573	0.18663605
C	-2.80556389	-1.24120005	0.04094139
C	-3.43884301	0.00866634	0.00043604
C	-4.92428112	0.01249599	0.00071174
C	-5.66511709	-0.46110759	-1.08417359
C	-7.05198747	-0.46842453	-1.10607411
H	-7.56545345	-0.84760490	-1.98276259
C	-7.73915218	0.01970497	0.00127849
H	-8.82493817	0.02247892	0.00150181
C	-7.04904631	0.50428634	1.10836281
H	-7.56021777	0.88604380	1.98527513
C	-5.66223678	0.48988584	1.08590399
C	-2.79923387	1.25530898	-0.04039739
C	-3.47440319	2.52848298	-0.12840010
H	-4.54565427	2.66170441	-0.18647095
C	-2.51592560	3.48972552	-0.14235344
H	-2.65124205	4.55991453	-0.21379343
C	-1.24269974	2.81533991	-0.06368754
C	0.00995753	3.44610491	-0.05631557
C	0.01754275	4.93098844	-0.09299708
C	-0.42586703	5.69747099	0.98667003
C	-0.43602089	7.08444297	0.97449260
H	-0.79081571	7.61892311	1.84882624
C	0.01757556	7.74473500	-0.16346656
H	0.01770415	8.83017596	-0.19058424
C	0.47082805	7.02831155	-1.26714879
H	0.82508893	7.51836673	-2.16735020
C	0.45992065	5.64249953	-1.20998495
O	-0.18895808	0.00770165	1.71188311