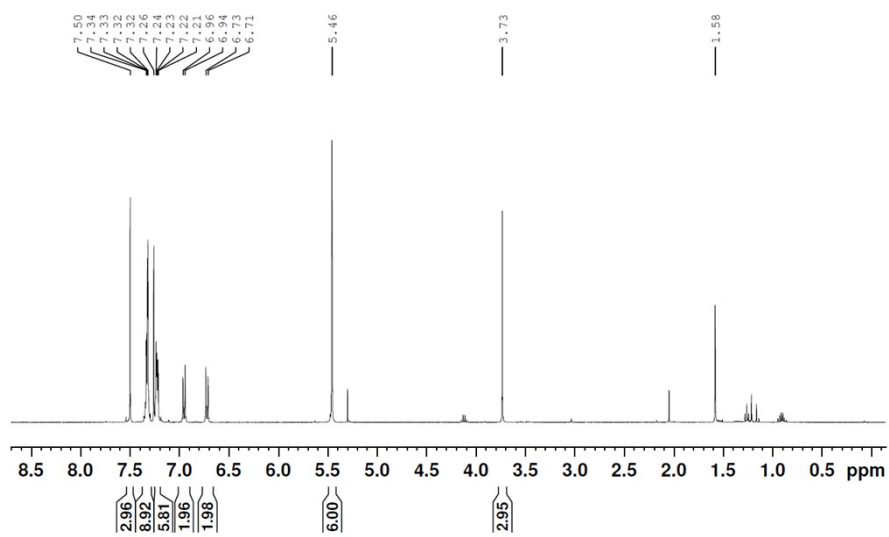


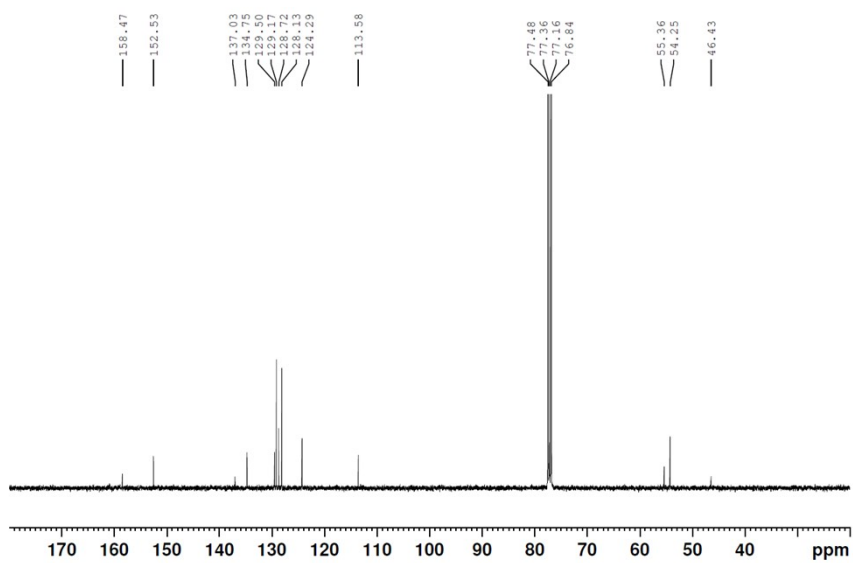
Supporting information for  
Synthesis and characterisation of group 8 tris(1-benzyl-1,2,3-triazol-4-yl)-p-  
anisolylmethane complexes

Samuel Francis, Craig R. Rice, Paul A. Scattergood & Paul I. P. Elliott\*

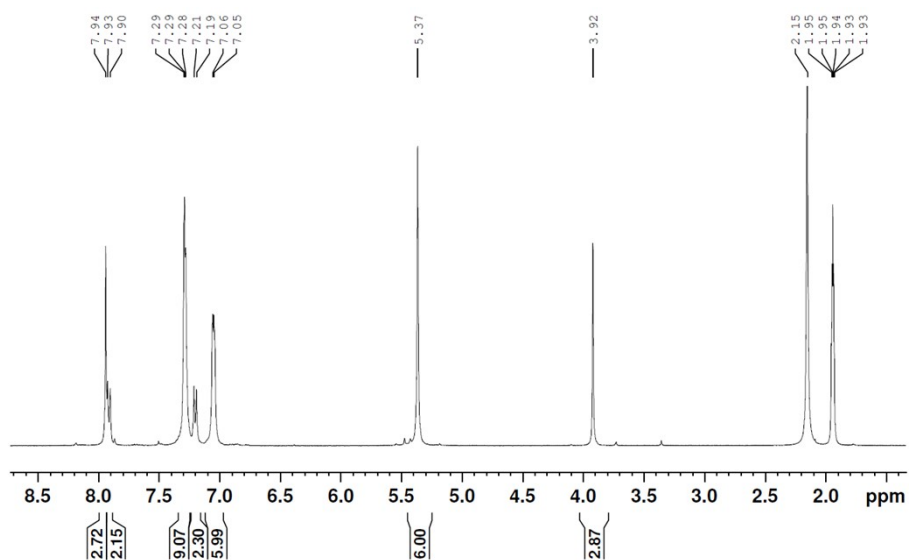
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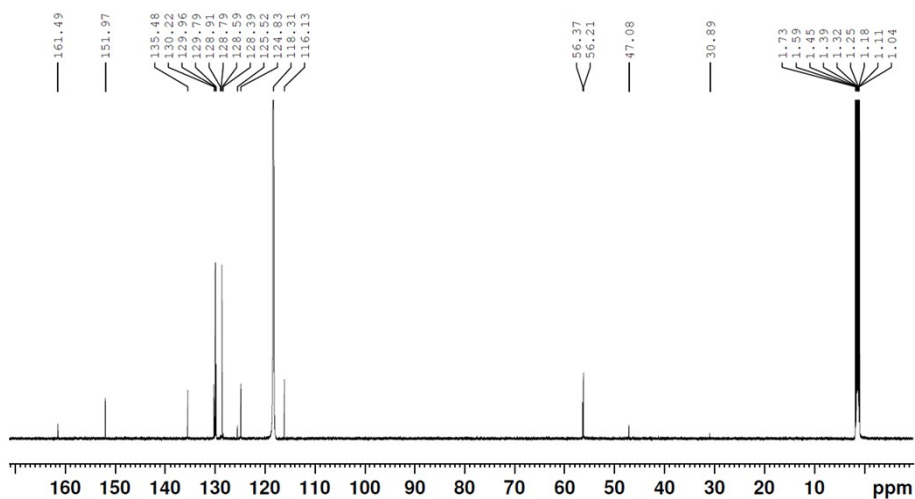
**Fig. S1.**  $^1\text{H}$  NMR spectrum of ttzm in  $\text{CDCl}_3$ .



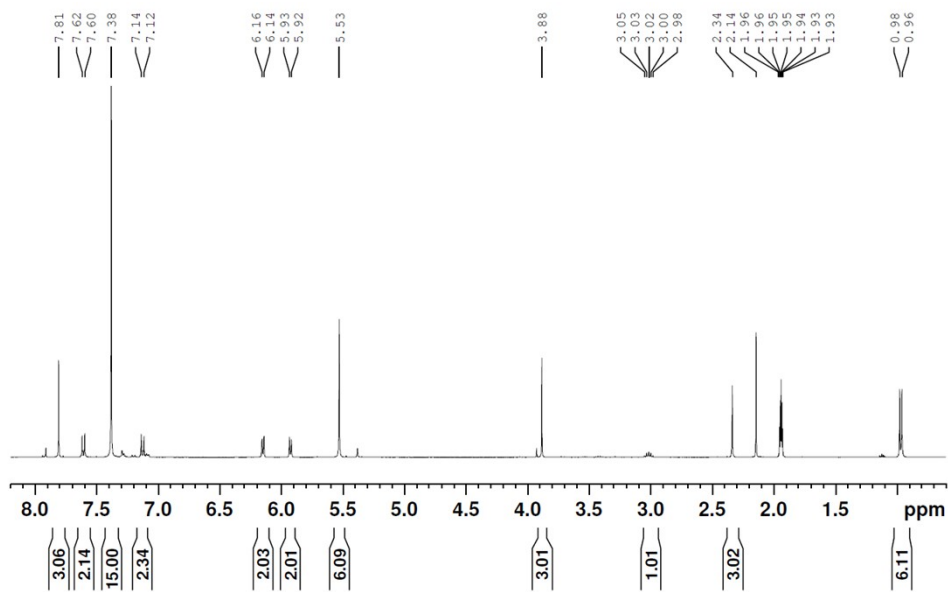
**Fig. S2.**  $^{13}\text{C}$  NMR spectrum of ttzm in  $\text{CDCl}_3$ .



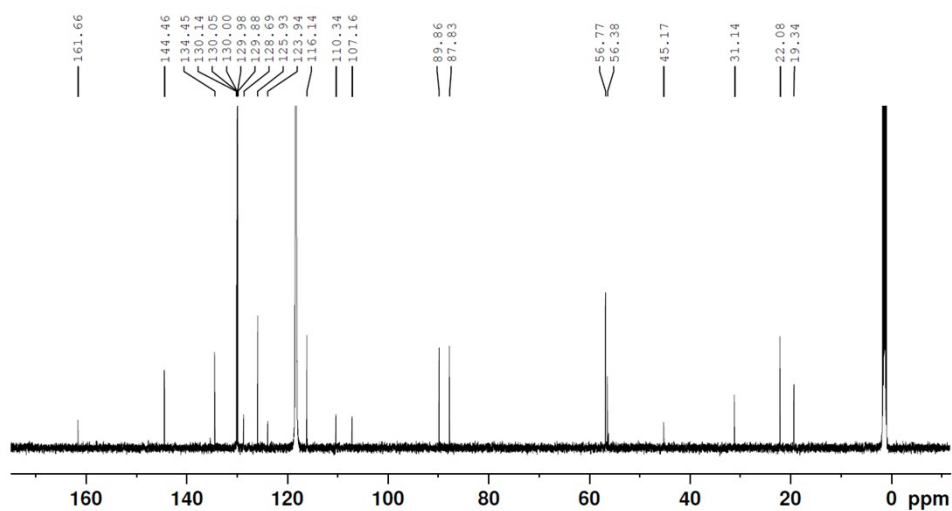
**Fig. S3.**  $^1\text{H}$  NMR spectrum of  $[\text{Fe}(\text{ttm})_2](\text{PF}_6)_2$  in  $\text{d}_3$ -acetonitrile.



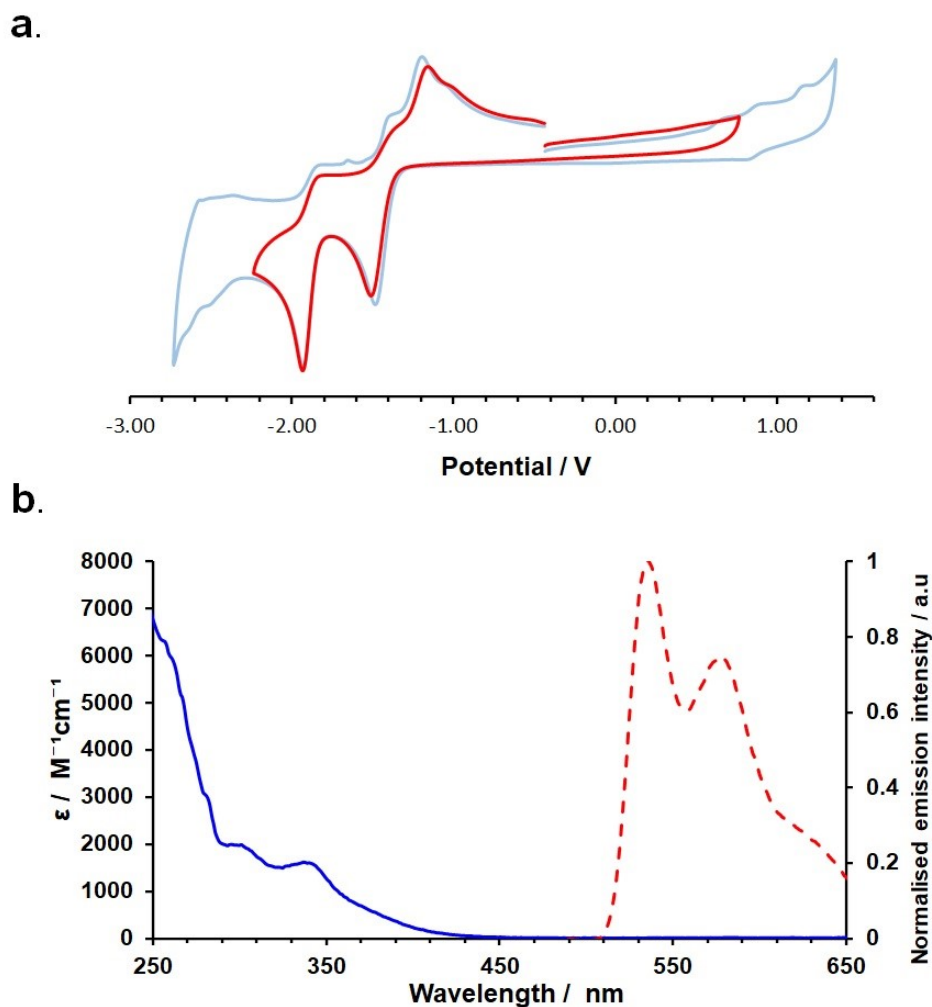
**Fig. S4.**  $^{13}\text{C}$  NMR spectrum of  $[\text{Fe}(\text{ttm})_2](\text{PF}_6)_2$  in  $\text{d}_3$ -acetonitrile.



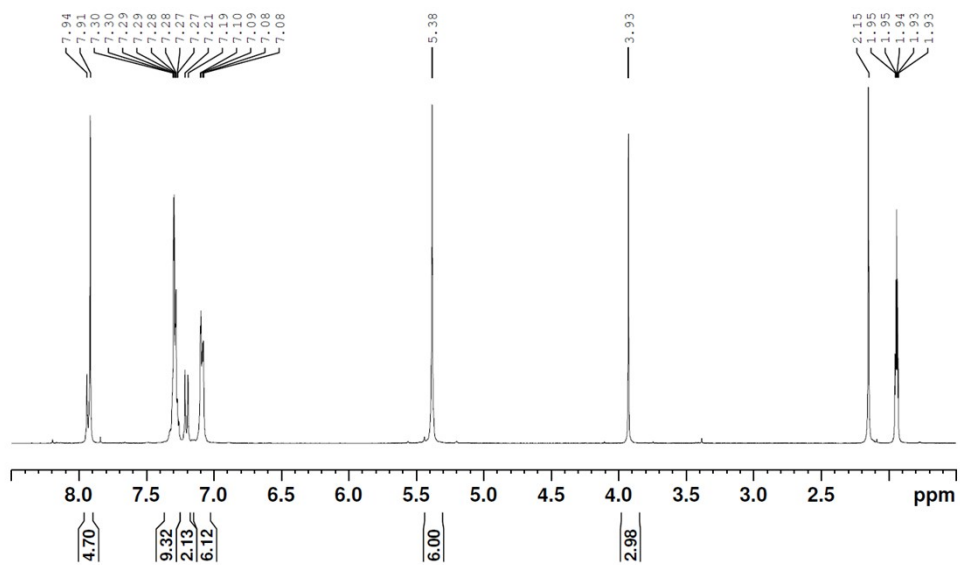
**Fig. S5.**  $^1\text{H}$  NMR spectrum of  $[\text{Ru}(p\text{-cymene})(\text{ttzm})](\text{PF}_6)_2$  in  $\text{d}_3$ -acetonitrile.



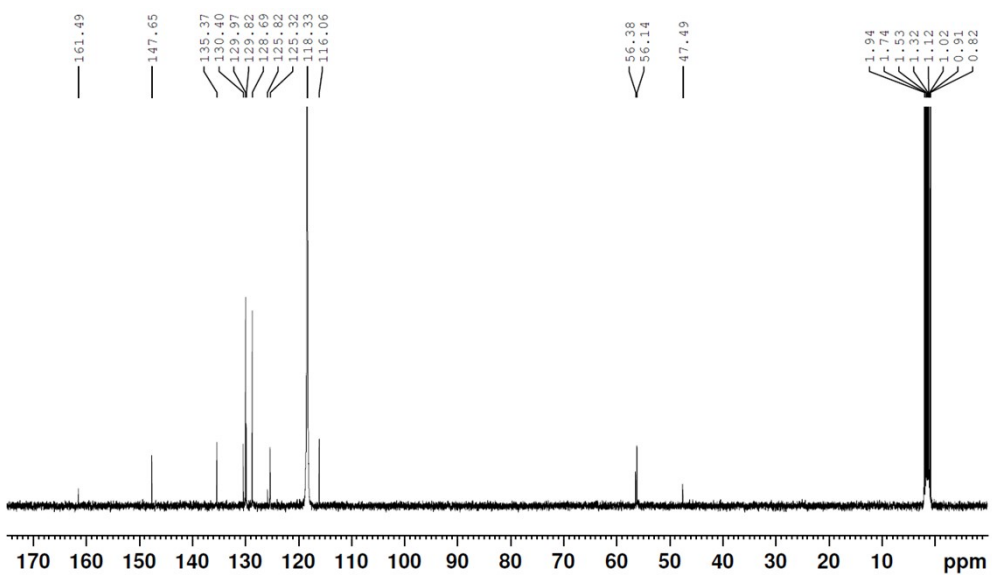
**Fig. S6.**  $^{13}\text{C}$  NMR spectrum of  $[\text{Ru}(p\text{-cymene})(\text{ttzm})](\text{PF}_6)_2$  in  $\text{d}_3$ -acetonitrile.



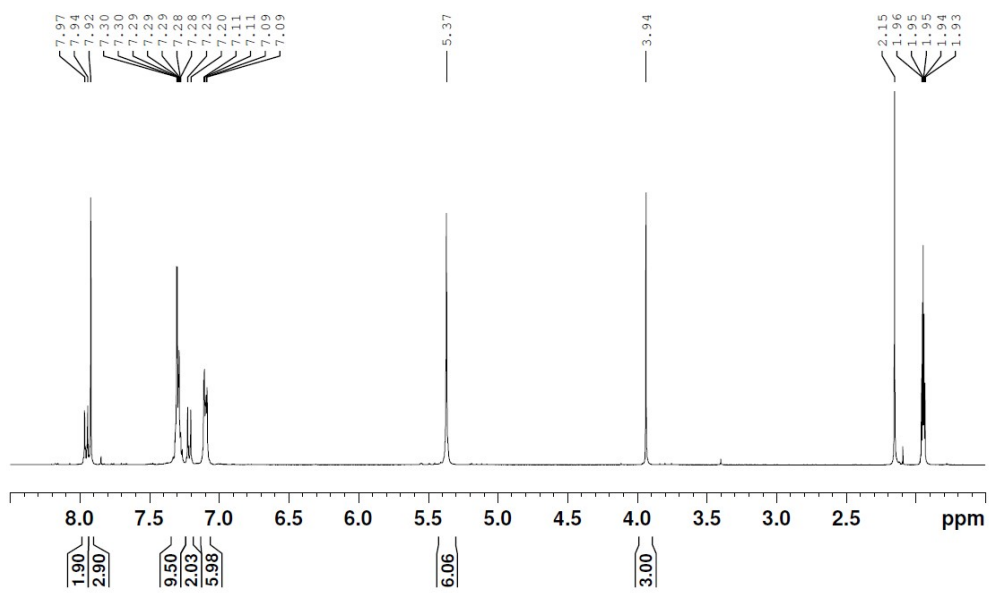
**Fig. S7.** (a) Cyclic voltammograms recorded for  $[\text{Ru}(p\text{-cymene})(\text{ttzm})](\text{PF}_6)_2$  at  $100 \text{ mVs}^{-1}$  in MeCN. (b) UV-Visible electronic absorption spectrum recorded for an MeCN solution of  $[\text{Ru}(p\text{-cymene})(\text{ttzm})](\text{PF}_6)_2$  at room temperature (blue, solid line) and 77 K luminescence spectrum recorded for  $[\text{Ru}(p\text{-cymene})(\text{ttzm})](\text{PF}_6)_2$  in a 4:1 EtOH/MeOH glass ( $\lambda_{\text{ex}} = 340 \text{ nm}$ ) (red, dashed line).



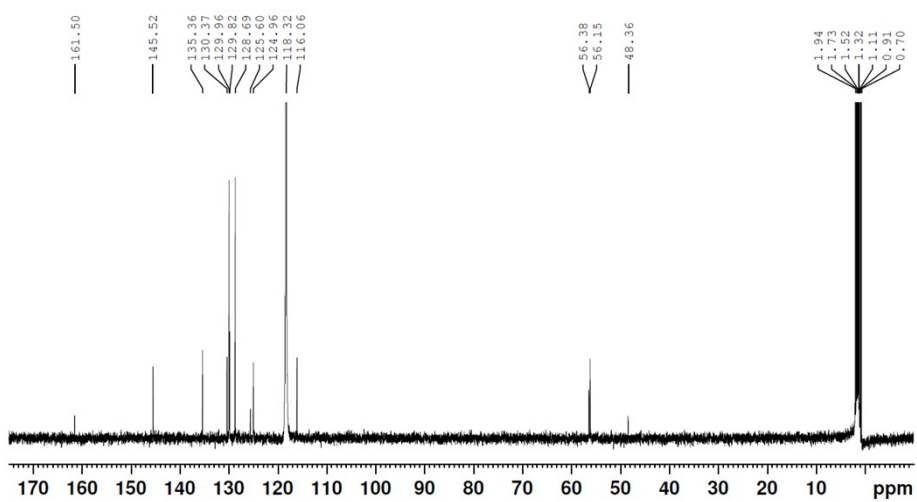
**Fig. S8.**  $^1\text{H}$  NMR spectrum of  $[\text{Ru}(\text{tzm})_2](\text{PF}_6)_2$  in  $\text{d}_3$ -acetonitrile.



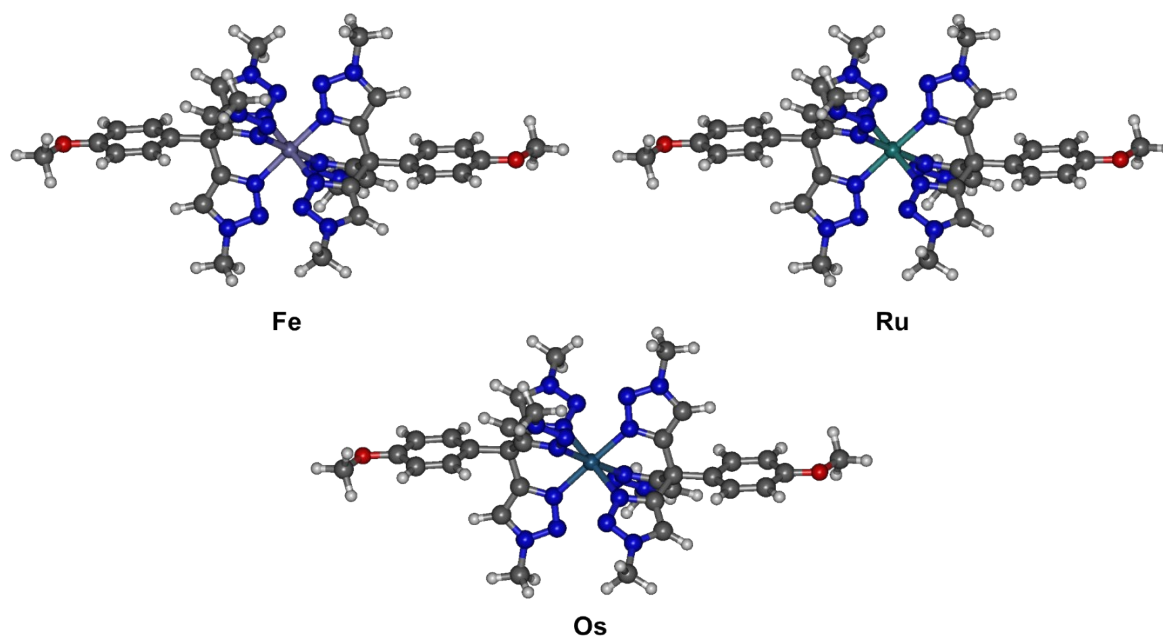
**Fig. S9.**  $^{13}\text{C}$  NMR spectrum of  $[\text{Ru}(\text{tzm})_2](\text{PF}_6)_2$  in  $\text{d}_3$ -acetonitrile.



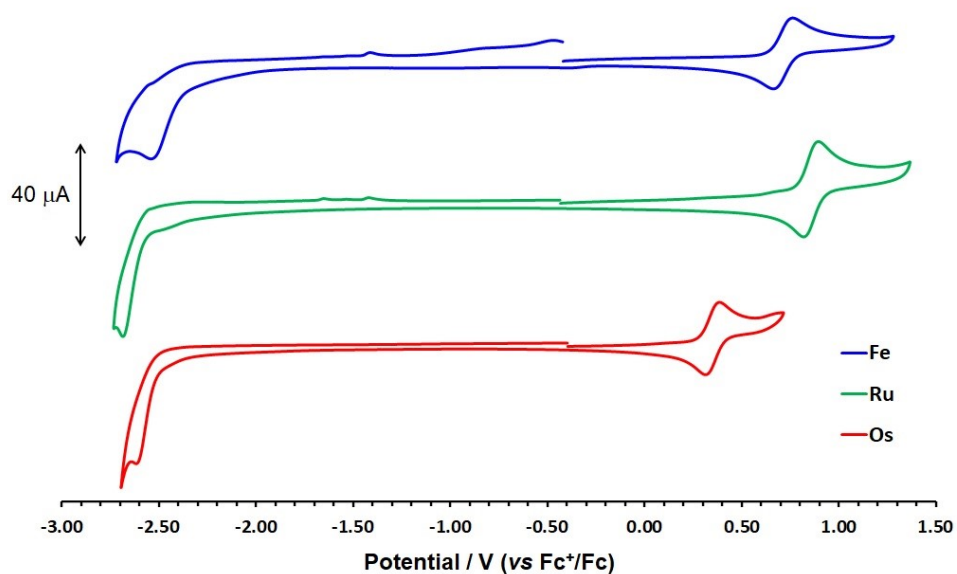
**Fig. S10.**  $^1\text{H}$  NMR spectrum of  $[\text{Os}(\text{ttzm})_2](\text{PF}_6)_2$  in  $\text{d}_3$ -acetonitrile.



**Fig. S11.**  $^{13}\text{C}$  NMR spectrum of  $[\text{Os}(\text{ttzm})_2](\text{PF}_6)_2$  in  $\text{d}_3$ -acetonitrile.

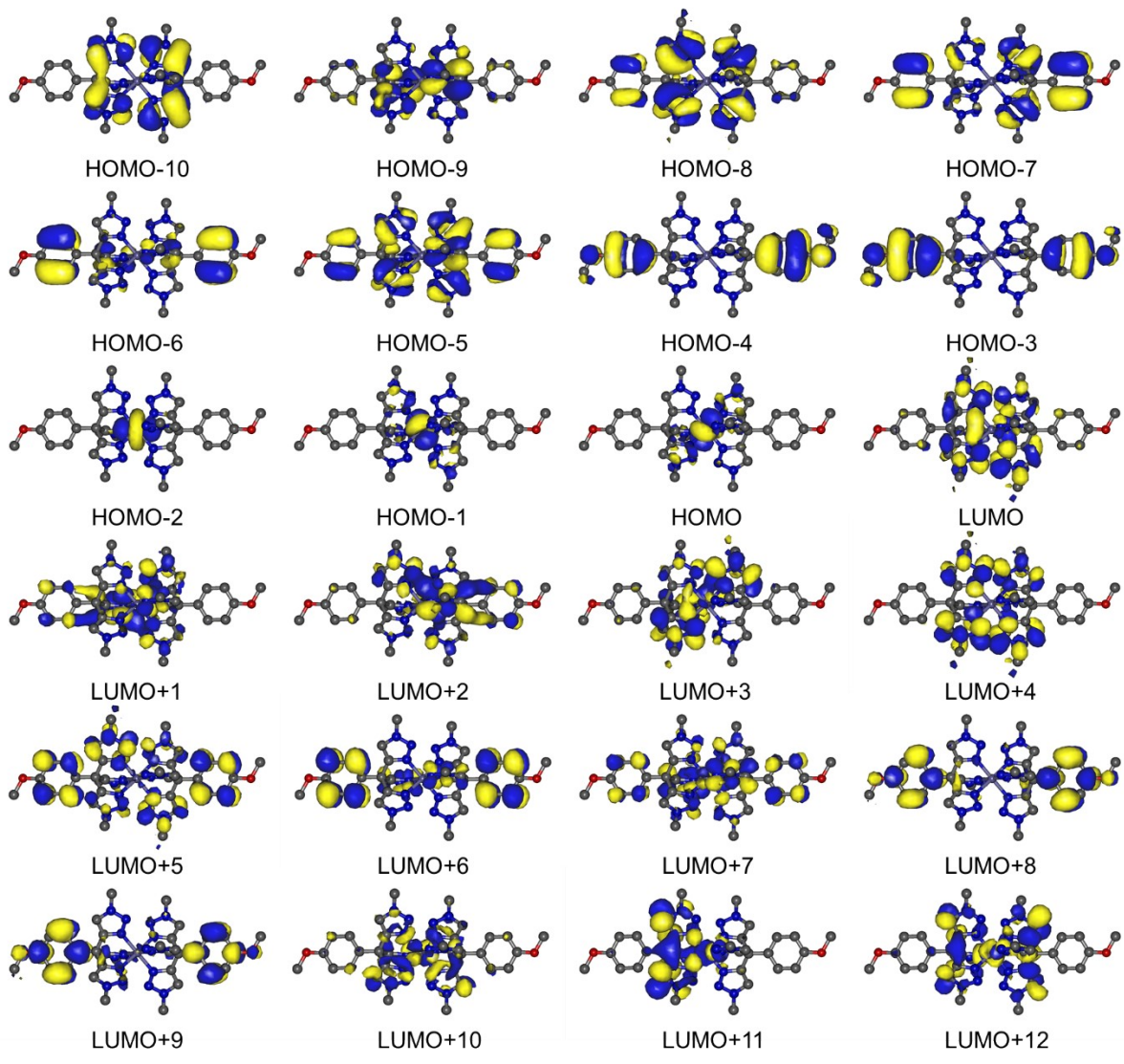


**Fig. S12.** Optimised ground state geometries of **Fe**, **Ru** and **Os** (benzyl substituents replaced by methyl).

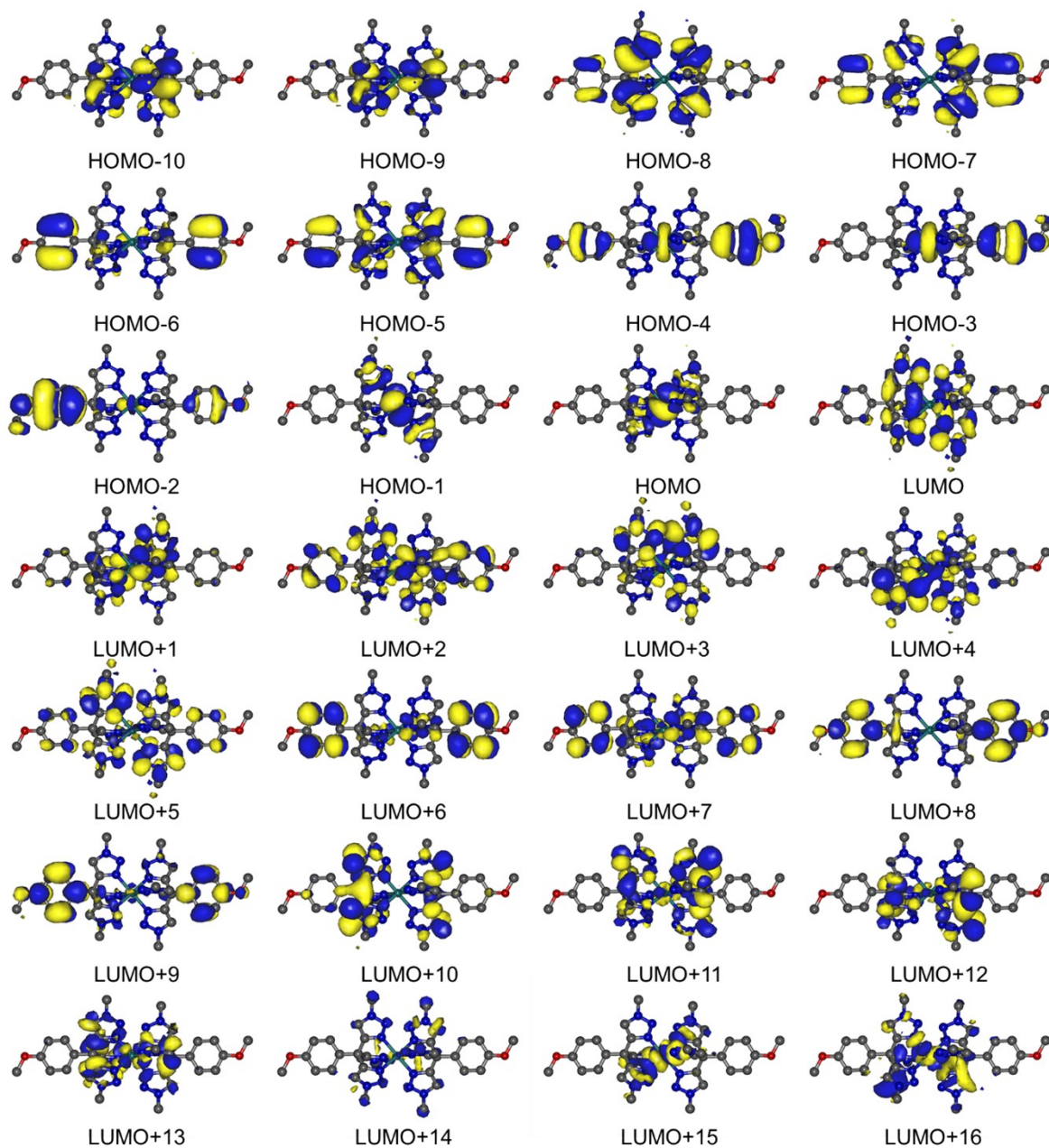


**Fig. S13.** Cyclic voltammetry traces for **Fe**, **Ru** and **Os** in acetonitrile recorded at  $100 \text{ mVs}^{-1}$  (calibrated against the Fc/Fc<sup>+</sup> couple for E = 0.0 V).

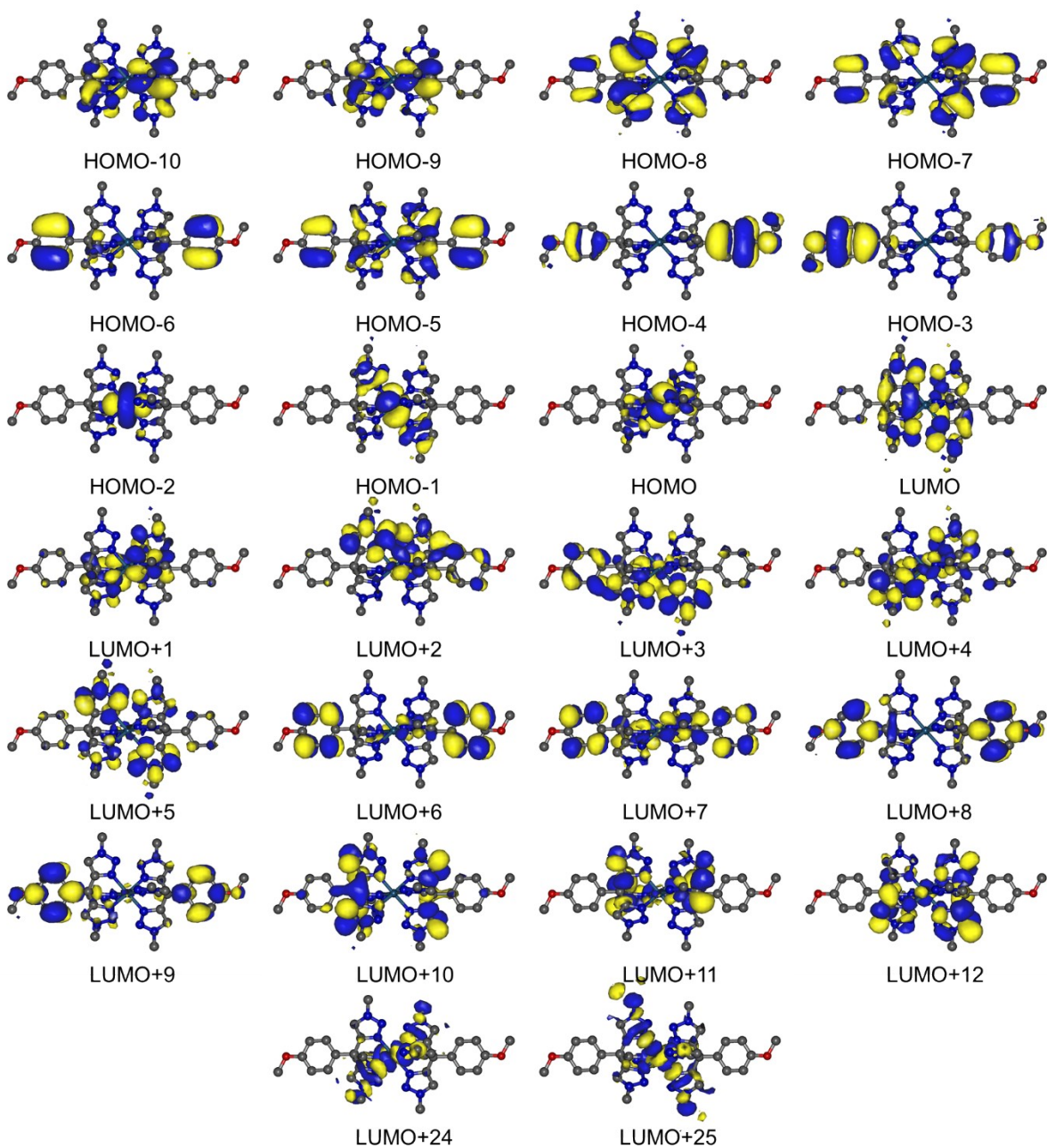




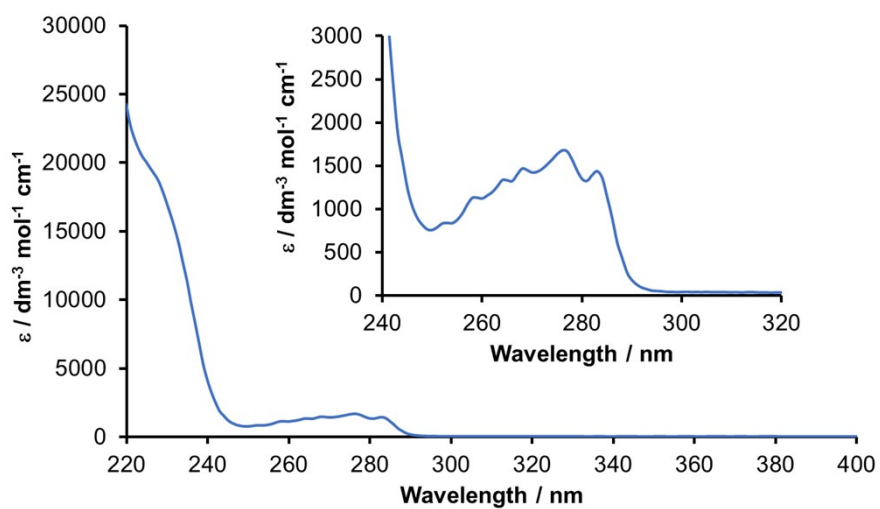
**Fig. S14.** Plots of selected orbitals for Fe (isosurface 0.02).



**Fig. S15.** Plots of selected orbitals for **Ru** (isosurface 0.02).

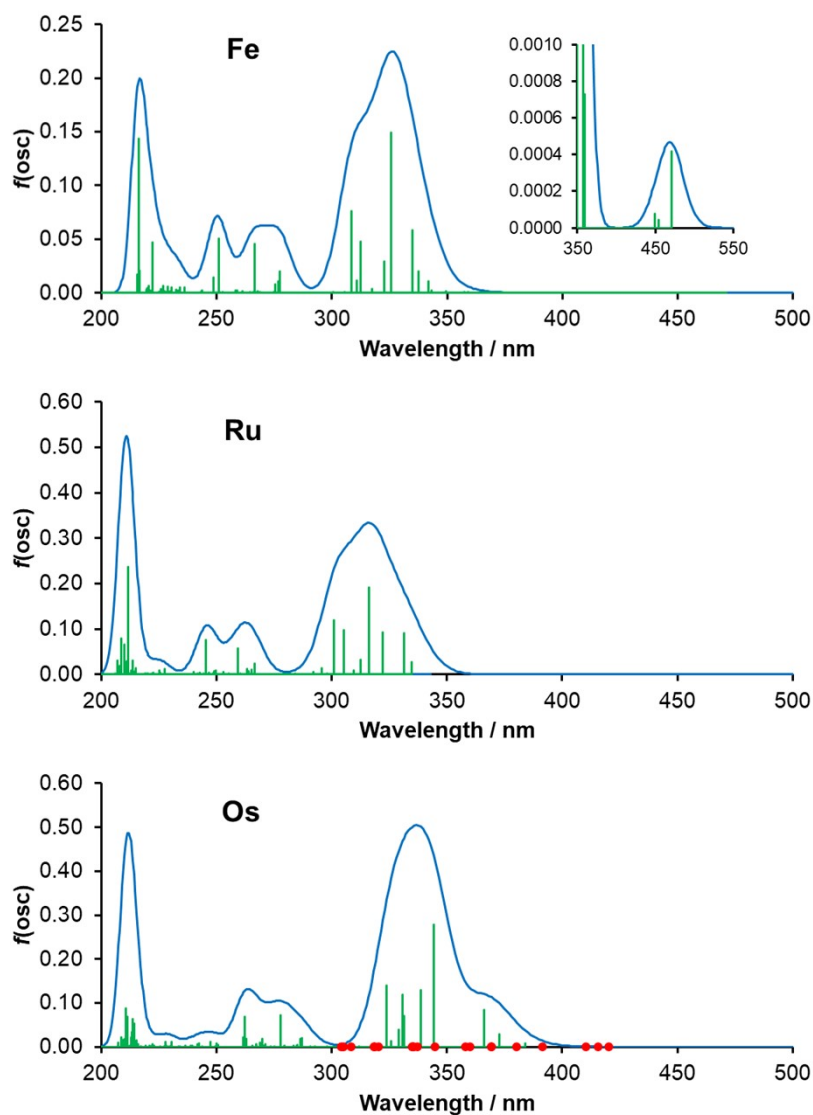


**Fig. S16.** Plots of selected orbitals for **Os** (isosurface 0.02).



**Fig. S17.** UV-visible absorption spectrum of free ttzm ligand in acetonitrile solution (inset: zoom of the region containing structured band apparent in spectra of complexes).





**Fig. S18.** TDDFT Calculated UV-visible absorption spectra for **Fe**, **Ru** & **Os**: positions of vertical excitations (green peaks) with Gaussian convolution (blue trace, FWHM = 0.1 eV). Red markers in the spectrum for **Os** show positions of spin-forbidden excitations of lowest 20 triplet states.

## Optimised ground state geometry for Fe

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Coordinates from ORCA-job gs

Fe	-0.00717886298096	0.01297821631572	0.00166292753086
N	-2.79351777722659	0.15714837815121	-2.90344876482949
N	-2.44131263323053	-0.05348513390114	-1.63649283505974
N	-1.16018532439425	0.21022911458127	-1.57053045179051
N	0.77217252960633	1.73515257508326	-0.49901201613591
N	1.06605649634793	2.76493781042508	0.25427600690221
N	1.56663934783035	3.69156053366668	-0.56677837658592
N	1.30602941811975	-0.79757522349990	-1.20625657096351
N	1.92692751885305	-1.93289783842244	-1.00982109403041
N	2.53701782290738	-2.22208581458532	-2.15643696337641
O	2.48230209975996	3.47336747471640	-7.69345255182851
C	-1.74137542447348	0.55118818156045	-3.65605836209214
H	-1.83720038100798	0.75201148861173	-4.70791294850125
C	-0.68007229767648	0.59952607006432	-2.78231908103959
C	0.80238410589684	0.94667080373044	-2.87855324595147
C	1.07851022418148	1.98631051426035	-1.79873339272780
C	1.59476547199112	3.25860629952177	-1.84789596117277
H	1.96238918907653	3.86592445479076	-2.65637009472219
C	1.98108537858298	4.98549678345220	-0.04328075158592
H	2.40564872052325	5.56294403199750	-0.86156975817403
H	2.73104408474855	4.83776305813974	0.73272635240370
C	1.52213839619714	-0.33574775310525	-2.47130508329389
C	2.31442473599977	-1.27309761748264	-3.09442444685216
H	2.71641797831999	-1.35524086623791	-4.08796288062237
C	3.33832314852149	-3.43234867236242	-2.26515009186329
H	3.59058719189076	-3.58472385045280	-3.31185791510547
H	2.75453459870902	-4.27427252805081	-1.89564215360561
C	1.20967583361946	1.54217606669667	-4.22160184044903
C	2.49095662799513	1.36289743438812	-4.75009899617643
H	3.21129333143325	0.73435280783100	-4.24600413789809
C	2.88710430586740	2.00988075475039	-5.90893271730580
H	3.88152746630255	1.85453887812563	-6.31117981509796
C	2.01291200473675	2.87888927646961	-6.56775356368446
C	0.74147404851559	3.09590298267701	-6.03501882080208
H	0.04739200317236	3.77929488153234	-6.50469179690915
C	0.36245485083163	2.43949438715785	-4.86977101810179
H	-0.61092600143996	2.66848053388703	-4.45728802535014
C	1.58600462673527	4.32500572903672	-8.41682599903488
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H	2.15109063832468	4.69352431483093	-9.27146649712635
H	1.25985543230895	5.17110107537394	-7.80480628728427
C	-4.18465592632978	0.01280839812728	-3.30357545203882
H	-4.25897747704367	0.23524297533686	-4.36601498469689
H	-4.79617554095712	0.71309541985878	-2.73610985565880
N	2.61406110667599	0.10341689017627	3.07726035485262
N	2.35326033471552	0.21802033142630	1.77434212197050
N	1.10963257303812	-0.16491389848157	1.61746281372769
N	-0.78419325853868	-1.71321104781589	0.46669438488594
N	-1.06717814628720	-2.72301428914683	-0.31715832863409
N	-1.59165555462292	-3.66425611003679	0.47081444759071
N	-1.34860307548840	0.81129048977792	1.18895595354887
N	-1.98934633343717	1.93083837124912	0.97344447265085
N	-2.69173435719895	2.17180010018845	2.07705199331629
O	-2.58684503737872	-3.59743303043476	7.59314188106054
C	1.54142350086484	-0.35690103563903	3.76039153199531
H	1.56117676621076	-0.50100847040318	4.82628553016124

C	0.56928096914731	-0.54569381596281	2.80801468843877
C	-0.89943767197992	-0.95535190202928	2.84564667731557
C	-1.12149123889998	-1.98958060609742	1.75131378180184
C	-1.64713797267243	-3.25962992629001	1.76069469077077
H	-2.03838091664951	-3.88236208821601	2.54602339841356
C	-2.00220479545144	-4.94196983503524	-0.09464592494262
H	-2.46240539371830	-5.53180838616469	0.69494311934975
H	-1.12948653905865	-5.46263290557786	-0.48881183619422
C	-1.63954949666329	0.31196872689894	2.42484427054905
C	-2.50842726541682	1.20659718551687	3.00739438817165
H	-2.98676882667195	1.25174304553003	3.96894919727740
C	-3.55787948040265	3.33924384165910	2.14100362793032
H	-4.45294921165265	3.16273479683578	1.54399199039615
H	-3.83321218949677	3.50945033993712	3.17907710984741
C	-1.31820146962760	-1.57851495668055	4.17166455062781
C	-2.61288080110127	-1.44540326693675	4.67901160274035
H	-3.34352261350270	-0.83247248279215	4.17043140956257
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H	-4.01406756920156	-2.00360718493924	6.20864276164821
C	-2.11905824251247	-2.97373572644849	6.48241176961544
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C	-0.45397361555172	-2.45897355587012	4.82058742857732
H	0.53521148985453	-2.64524449772725	4.42292869194750
C	-1.68247907598474	-4.45077756013431	8.30468681907695
H	-0.82443015717048	-3.88434443216792	8.67820828512845
H	-2.25001904580390	-4.85180989401760	9.14290776402091
H	-1.33436029589387	-5.27466458567850	7.67456222203281
C	3.93418765026637	0.42551380294964	3.60047913036433
H	4.50537063910962	0.88993400595868	2.79957643253170
H	4.42898332301997	-0.48552772964709	3.93715833569575
H	1.11561736122550	5.50363774709869	0.36973882238634
H	4.24908261762258	-3.32201534774186	-1.67672820921304
H	-4.51320347302615	-1.00815562084001	-3.10961954364390
H	-2.72180442401461	-4.76656187820748	-0.89327170130088
H	-3.01372733065816	4.19868884946958	1.75276017575163
H	3.83024618650075	1.11998968004489	4.43332296761936

## Optimised ground state geometry for Ru

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Coordinates from ORCA-job gs

Ru	0.00075239154264	0.00035972032611	-0.00001392487812
N	-2.78032569179895	0.23542827877170	-3.02203822649033
N	-2.45276262606423	-0.00608561058574	-1.75580538931798
N	-1.16629989073675	0.22001263611821	-1.66938543674855
N	0.82272721943584	1.78828905626248	-0.57417659467922
N	1.11788101918753	2.83913711669273	0.14791028191916
N	1.61254289528026	3.74119954031510	-0.70184543330052
N	1.35904980662372	-0.82823799156488	-1.29794661283138
N	1.96914057367080	-1.97389287308560	-1.13422841670787
N	2.54659918153484	-2.25145026598570	-2.29823301679597
O	2.52607218269250	3.51400793625000	-7.74305656256356
C	-1.70847494462038	0.60772199881939	-3.75304010212667
H	-1.78497561484973	0.82607102783631	-4.80107675729243
C	-0.65592425127016	0.61502801815149	-2.86822244303887
C	0.83383106767950	0.94682067431643	-2.95177036886173
C	1.12190269799337	2.00030927913574	-1.88364665438687
C	1.63463203371810	3.27198078330372	-1.96739091921810
H	1.99676261486700	3.85713242648453	-2.79216327267433
C	2.02885435385075	5.05069189614235	-0.21815766426744
H	2.44405410558500	5.60477811215755	-1.05512687491775
H	2.78537672408698	4.92620207806766	0.55333822344606
C	1.55028389193242	-0.34604838212632	-2.56107124602397
C	2.31394977692602	-1.28654438338739	-3.21416743536145
H	2.68947902093840	-1.36054725405727	-4.21683305325972
C	3.31649684702168	-3.47878122389665	-2.44584964606434
H	3.57545153171512	-3.59781865265824	-3.49365784555196
H	2.70666591363345	-4.31623594494871	-2.11434058928163
C	1.24275805126960	1.54624374490282	-4.29644159212720
C	2.51605059754646	1.35428250593439	-4.83674391081997
H	3.22970301384228	0.70922905628194	-4.34863571204847
C	2.91502268392750	2.01185713254305	-5.98818819747301
H	3.90250173631118	1.84479000216855	-6.39824254104224
C	2.05371757211579	2.90683662440588	-6.62638527410467
C	0.79082871708411	3.13631915099483	-6.08171190943594
H	0.10637594445078	3.83878739221162	-6.53301116175873
C	0.40938481475942	2.46932648298441	-4.92462183897786
H	-0.55320395729941	2.71360237238348	-4.50106220135533
C	1.63738076997216	4.38313551316099	-8.45282105076768
H	0.76391177911726	3.83475071460716	-8.81257957498950
H	2.20558411974793	4.76263535417616	-9.29859115298246
H	1.31533034431267	5.21958959336586	-7.82858346659270
C	-4.17302813022573	0.15762553803047	-3.43542171028525
H	-4.22836075527078	0.39503272243467	-4.49421859885475
H	-4.75549280010541	0.87767458686363	-2.86520284602413
N	2.55311317917666	0.13942794386391	3.24787501179722
N	2.35038513261353	0.22917743821108	1.93449621478373
N	1.12014818130686	-0.17402339172778	1.72928403476560
N	-0.81569235747648	-1.79213783870909	0.53736286596533
N	-1.09312845748505	-2.82553675461639	-0.21595488385617
N	-1.60799129715729	-3.74576335082237	0.60096596758580
N	-1.40726309865328	0.80501896146513	1.25852915394811
N	-2.06267647695046	1.91675200083998	1.05260162387229
N	-2.76775619823378	2.13659396038606	2.15624241779730
O	-2.53097695017238	-3.64406209121223	7.67767452921991
C	1.45946876408414	-0.32507774165745	3.88889785304243
H	1.43365748837751	-0.45266325544214	4.95505802495764



C	0.53164384968982	-0.54503498018588	2.90100956984962
C	-0.93493478420056	-0.97416127856264	2.91122945884425
C	-1.14668862032965	-2.03093152296809	1.83233571361712
C	-1.66227867145915	-3.30406545591153	1.87610441628882
H	-2.04613902702961	-3.90693526712068	2.67799615378267
C	-2.01239337749448	-5.04291000561308	0.07480942439704
H	-2.45290199865705	-5.61618133423902	0.88541013152286
H	-1.14095999370138	-5.56189743983320	-0.31997472880128
C	-1.69203714990876	0.28631296566406	2.49024913927203
C	-2.57238960992077	1.16711199752757	3.07626725836495
H	-3.05116465768135	1.20211304110695	4.03594823442209
C	-3.64882835113727	3.29256217387742	2.22708463810092
H	-4.53560319489189	3.11052563137362	1.62233296990943
H	-3.93359738778872	3.44784229659647	3.26331966671431
C	-1.34018921475856	-1.60271110163239	4.24286700615701
C	-2.61540744671114	-1.45819827455624	4.79013765926922
H	-3.35400519911112	-0.83357963001148	4.31303800903847
C	-2.98459051934152	-2.14128735592763	5.93782505832724
H	-3.97481887199102	-2.01265634186762	6.35511929769043
C	-2.08983654178940	-3.01359571992244	6.56089316262090
C	-0.82348646665799	-3.19681719438990	6.00563005272080
H	-0.11325963592606	-3.88016634567831	6.44619462384033
C	-0.47140321022627	-2.50407342675316	4.85533513285221
H	0.50116566385123	-2.69959282181457	4.42656526410728
C	-1.61895183968525	-4.51749790522599	8.35167979643898
H	-0.74838103478512	-3.96607053233900	8.71347078754411
H	-2.16951898027920	-4.92790913162814	9.19467685961390
H	-1.29387342185543	-5.33233053993239	7.70072643164236
C	3.84766162480938	0.47818710926810	3.82400343892366
H	4.44183580877951	0.95585997249763	3.05028448271503
H	4.34125411863937	-0.42627891525216	4.17476820101569
H	1.16708968188179	5.57641383434910	0.18883747620748
H	4.22160739587894	-3.41535832262694	-1.84533657288626
H	-4.54739658342966	-0.84800664380452	-3.25371861976911
H	-2.74557224886930	-4.89744762219089	-0.71534971858019
H	-3.11238450373727	4.16054063961755	1.85174874553464
H	3.70002217826334	1.16443673422586	4.65457408472725

## Optimised ground state geometry for Os

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Coordinates from ORCA-job gs

Os	5.18140448358479	5.74554447693820	6.41516379790128
N	2.40278656765023	5.99279528048573	3.38043481766428
N	2.72718407000228	5.74667283992961	4.64673895509539
N	4.01807194817231	5.96939279851743	4.73459844742403
N	6.00805694837738	7.53566371823649	5.82813149935141
N	6.30536065240028	8.58913892802151	6.55225083216526
N	6.80198735408270	9.48890992684926	5.70074947764808
N	6.53740740205158	4.91673016664322	5.10320737845990
N	7.15503706971468	3.77100702776744	5.26744090256831
N	7.73848577799662	3.50100192982881	4.10456082454107
O	7.70983834558878	9.26365423048310	-1.34308857965827
C	3.47529675291337	6.36332449852239	2.65065460861923
H	3.39898322312126	6.58413441374216	1.60311993570637
C	4.52920100366539	6.36655456767052	3.53328817638464
C	6.01915023514535	6.69631146751175	3.44912508538045
C	6.30914708335061	7.74971159176281	4.51646529827220
C	6.82433348403927	9.01988577548644	4.43556606379090
H	7.18803123799523	9.60483128538116	3.61129381636878
C	7.21974881105021	10.79778420053487	6.18399256448456
H	7.63288867033582	11.35228115584354	5.34626301298758
H	7.97818697501007	10.67304850284244	6.95367810691424
C	6.73583717929221	5.40372663997982	3.83955971531233
C	7.50630739681912	4.46677064394268	3.19026679126898
H	7.88746386479039	4.39606531657670	2.18953007077910
C	8.51528361856664	2.27822905624777	3.95810078705594
H	8.77997346684911	2.16256572020743	2.91134116573096
H	7.90824049193178	1.43695965103324	4.28526691919599
C	6.42771052234496	7.29621571859379	2.10433166510188
C	7.70062954999153	7.10398932677531	1.56318934357196
H	8.41474181995112	6.45926440049734	2.05095283710266
C	8.09920385009982	7.76149080421649	0.41157862889282
H	9.08644772335635	7.59409715175729	0.00109329423895
C	7.23795132077065	8.65689599585722	-0.22603700919882
C	5.97563498459542	8.88705362765938	0.31968041555858
H	5.29127457739065	9.59000893689969	-0.13100717805591
C	5.59460798779332	8.22015050510728	1.47699495683210
H	4.63264725332776	8.46513429231236	1.90138843780292
C	6.82118955305164	10.13302116272104	-2.05262250283886
H	5.94733021275588	9.58492039424248	-2.41185673815096
H	7.38919634016253	10.51206645578740	-2.89873056851494
H	6.49982980941594	10.96977142846468	-1.42844351341110
C	1.00986019453147	5.92262214908891	2.96731103519813
H	0.95539708656678	6.16101048259560	1.90867881230797
H	0.43169197567885	6.64532560861992	3.53876657344349
N	7.73383994984420	5.87502075049701	9.67277218549621
N	7.53122359110152	5.97072772802546	8.35979606906144
N	6.29569191659102	5.57178792489784	8.15471142984799
N	4.36066615002721	3.94981074085134	6.96698441362872
N	4.08039162533925	2.91347467006671	6.21220593235669
N	3.56424648538291	1.99581963310655	7.03180460947632
N	3.77263561278973	6.54845722857336	7.68608894531531
N	3.10826802099733	7.65887701918745	7.47816447695702
N	2.39897962277978	7.87173175271573	8.58056204443110
O	2.65056232024203	2.09888351519152	14.10983439688004
C	6.64083522907793	5.41097371874234	10.31403223159549
H	6.61734927561127	5.27981421526591	11.37980631122288

C	5.70927023747987	5.19568799654674	9.32921430205611
C	4.24250440806038	4.76772714937763	9.34130920304719
C	4.02856201097278	3.70958981633987	8.26439881304289
C	3.51090691787309	2.43793802387558	8.30643446668014
H	3.12618981587468	1.83566463304375	9.10841620307141
C	3.15799327980276	0.69910552296687	6.50681121774008
H	2.71918681712966	0.12604635649099	7.31849295673701
H	4.02827141673167	0.17973277010933	6.10979677225185
C	3.48434884251770	6.02697064468940	8.91938887459342
C	2.59721634832828	6.90367945164700	9.50061298745539
H	2.11463447243445	6.93602691846268	10.45848840767625
C	1.50978929815525	9.02135044286655	8.64812774299144
H	0.62888099596173	8.83498597257073	8.03606821874788
H	1.21607016272990	9.17169662984817	9.68257744132311
C	3.83852992208638	4.13998886252068	10.67383303454387
C	2.56306106838150	4.28289890434852	11.22099263418828
H	1.82330979290027	4.90559909861514	10.74328831828499
C	2.19481436424334	3.59996720415552	12.36903871255283
H	1.20428750276696	3.72731106315023	12.78600646251651
C	3.09074694720300	2.72925673071021	12.99268661596031
C	4.35727448666815	2.54743197899930	12.43744526681848
H	5.06848398152492	1.86530178485559	12.87828595948206
C	4.70836751900832	3.23993422704214	11.28669553815138
H	5.68103037400574	3.04511002971747	10.85806102355209
C	3.56353331546352	1.22633254093374	14.78379058385418
H	4.43351655305467	1.77866547406163	15.14558802678408
H	3.01337146995823	0.81528860880955	15.62673689781290
H	3.88942247777495	0.41189393285447	14.13275027696217
C	9.03049120779133	6.20690326637171	10.24800447752490
H	9.62429169586216	6.68756705790450	9.47585732249378
H	9.52252179258204	5.29908171369802	10.59228510046804
H	6.35903319179786	11.32338829033215	6.59355253193763
H	9.41723538873555	2.34521575440494	4.56312931152954
H	0.63008663430671	4.91891820970423	3.14874581845151
H	2.42300805894984	0.84465913124322	5.71822943088348
H	2.04297746874218	9.89412099870920	8.27911421156653
H	8.88645108607325	6.88864965871799	11.08291282870234

**Table S1.** Selected TDDFT transitions for **Fe** and their dominant composition and character.

State	Energy / cm <sup>-1</sup>	$\lambda$ / nm	$f(\text{osc})$	Composition	Character
S <sub>1</sub>	21224	471	0.000416	HOMO→LUMO+10 (27 %) HOMO-1→LUMO+10 (13 %)	<sup>1</sup> MC
S <sub>8</sub>	29259	342	0.0106	HOMO→LUMO (46 %) HOMO-1→LUMO (16 %)	<sup>1</sup> MLCT (tz)
S <sub>9</sub>	29616	338	0.0202	HOMO-1→LUMO (32 %) HOMO→LUMO+1 (29 %)	<sup>1</sup> MLCT (tz)
S <sub>10</sub>	29869	335	0.0587	HOMO-1→LUMO+1 (31 %) HOMO→LUMO (25 %) HOMO-1→LUMO (17 %)	<sup>1</sup> MLCT (tz)
S <sub>11</sub>	30710	326	0.149	HOMO→LUMO+1 (31 %) HOMO-1→LUMO+1 (28 %) HOMO-1→LUMO (14 %)	<sup>1</sup> MLCT (tz)
S <sub>12</sub>	31005	323	0.0294	HOMO-1→LUMO+2 (29 %) HOMO→LUMO+3 (28 %) HOMO-2→LUMO+2 (14 %)	<sup>1</sup> MLCT (tz)
S <sub>14</sub>	32020	312	0.0476	HOMO→LUMO+4 (38 %) HOMO-1→LUMO+4 (37 %) HOMO-2→LUMO (16 %)	<sup>1</sup> MLCT (tz)
S <sub>15</sub>	32188	311	0.0114	HOMO-2→LUMO (72 %)	<sup>1</sup> MLCT (tz)
S <sub>16</sub>	32424	308	0.0758	HOMO-1→LUMO+4 (47 %) HOMO→LUMO+4 (42 %)	<sup>1</sup> MLCT (tz)
S <sub>25</sub>	36048	277	0.0201	HOMO-4→LUMO (52 %) HOMO-3→LUMO (16 %) HOMO→LUMO+6 (11 %)	<sup>1</sup> ILCT (An→tz) <sup>1</sup> MLCT (An)
S <sub>27</sub>	36127	277	0.0111	HOMO-1→LUMO+6 (71 %) HOMO→LUMO+6 (22 %)	<sup>1</sup> MLCT (An)
S <sub>37</sub>	37550	266	0.0454	HOMO-1→LUMO+8 (44 %) HOMO→LUMO+8 (28 %)	<sup>1</sup> MLCT (An)
S <sub>51</sub>	39870	251	0.0504	HOMO-1→LUMO+14 (66 %) HOMO→LUMO+14 (28 %)	<sup>1</sup> MLCT (tz)
S <sub>52</sub>	40228	249	0.0144	HOMO-3→LUMO+5 (48 %) HOMO-4→LUMO+6 (52 %)	<sup>1</sup> ILCT (An→tz) <sup>1</sup> LC (An)
S <sub>89</sub>	45028	222	0.0471	HOMO-5→LUMO+4 (77 %)	<sup>1</sup> ILCT (An→tz) <sup>1</sup> LC (tz)
S <sub>98</sub>	46212	216	0.0208	HOMO-5→LUMO+5 (30 %) HOMO-8→LUMO+4 (28 %) HOMO-7→LUMO+4 (13 %)	<sup>1</sup> LC
S <sub>99</sub>	46288	216	0.143	HOMO-7→LUMO+4 (37 %) HOMO-6→LUMO+5 (11 %) HOMO-3→LUMO+9 (77 %)	<sup>1</sup> LC
T <sub>1</sub>	15587	642	-	HOMO→LUMO+10 (35 %) HOMO-1→LUMO+10 (13 %)	<sup>3</sup> MC
T <sub>2</sub>	16165	619	-	HOMO-2→LUMO+10 (27 %)	<sup>3</sup> MC
T <sub>3</sub>	16268	615	-	HOMO-1→LUMO+11 (17 %) HOMO-1→LUMO+12 (17 %) HOMO-1→LUMO+13 (16 %)	<sup>3</sup> MC
T <sub>7</sub>	26288	380	-	HOMO→LUMO+3 (32 %) HOMO-1→LUMO+2 (31 %) HOMO-1→LUMO+1 (15 %)	<sup>3</sup> MLCT

**Table S2.** Selected TDDFT transitions for **Ru** and their dominant composition and character.

State	Energy / cm <sup>-1</sup>	$\lambda$ / nm	$f(\text{osc})$	Composition	Character
S <sub>1</sub>	29178	343	0.0107	HOMO→LUMO (72 %)	<sup>1</sup> MLCT (tz)
S <sub>2</sub>	29885	335	0.0268	HOMO-1→LUMO+1 (17 %) HOMO-1→LUMO (34 %) HOMO→LUMO+1 (24 %)	<sup>1</sup> MLCT (tz)
S <sub>3</sub>	30173	331	0.0915	HOMO-1→LUMO+1 (38 %) HOMO-1→LUMO (28 %) HOMO→LUMO (20 %)	<sup>1</sup> MLCT (tz)
S <sub>4</sub>	31051	322	0.0933	HOMO→LUMO+2 (36 %) HOMO→LUMO+1 (26 %) HOMO-1→LUMO (11 %)	<sup>1</sup> MLCT (tz + An)
S <sub>5</sub>	31627	316	0.192	HOMO→LUMO+1 (36 %) HOMO→LUMO+2 (28 %) HOMO-1→LUMO (14 %)	<sup>1</sup> MLCT (tz + An)
S <sub>6</sub>	32007	312	0.0329	HOMO-1→LUMO+2 (45 %) HOMO-1→LUMO+4 (30 %)	<sup>1</sup> MLCT (tz + An)
S <sub>8</sub>	32763	305	0.0984	HOMO→LUMO+3 (61 %) HOMO→LUMO+4 (11 %)	<sup>1</sup> MLCT (tz)
S <sub>9</sub>	33233	301	0.12	HOMO-1→LUMO+3 (53 %) HOMO-1→LUMO+4 (24 %) HOMO→LUMO+3 (10 %)	<sup>1</sup> MLCT (tz)
S <sub>11</sub>	33844	296	0.0133	HOMO-1→LUMO+5 (16 %) HOMO-3→LUMO+1 (14 %)	<sup>1</sup> MLCT (tz) <sup>1</sup> ILCT (An→tz)
S <sub>21</sub>	37512	267	0.0235	HOMO→LUMO+6 (38 %) HOMO-1→LUMO+6 (27 %) HOMO-2→LUMO (12 %)	<sup>1</sup> MLCT (An)
S <sub>22</sub>	37533	266	0.022	HOMO→LUMO+6 (40 %) HOMO-1→LUMO+6 (38 %)	<sup>1</sup> MLCT (An)
S <sub>24</sub>	37722	265	0.0102	HOMO-4→LUMO (38 %) HOMO-3→LUMO (30 %)	<sup>1</sup> MLCT (tz) <sup>1</sup> ILCT (An→tz)
S <sub>28</sub>	38009	263	0.0121	HOMO-2→LUMO+1 (49 %) HOMO-4→LUMO+1 (16 %)	<sup>1</sup> MLCT (tz) <sup>1</sup> ILCT (An→tz)
S <sub>30</sub>	38603	259	0.0572	HOMO-1→LUMO+8 (48 %) HOMO-1→LUMO+10 (24 %) HOMO→LUMO+8 (14 %)	<sup>1</sup> MLCT (An + tz)
S <sub>44</sub>	40763	245	0.0761	HOMO→LUMO+12 (43 %) HOMO-1→LUMO+12 (36 %)	<sup>1</sup> MLCT (tz)
S <sub>57</sub>	43970	227	0.0119	HOMO-5→LUMO (86 %)	<sup>1</sup> ILCT (An→tz) <sup>1</sup> LC (tz)
S <sub>77</sub>	46557	215	0.0139	HOMO-6→LUMO+2 (28 %) HOMO-5→LUMO+3 (14 %) HOMO-8→LUMO+2 (11 %)	<sup>1</sup> LC
S <sub>82</sub>	46840	214	0.0311	HOMO-5→LUMO+3 (50 %) HOMO-6→LUMO+2 (16 %)	<sup>1</sup> LC
S <sub>87</sub>	47249	212	0.0561	HOMO-1→LUMO+16 (16 %) HOMO→LUMO+16 (19 %) HOMO-1→LUMO+17 (16 %) HOMO→LUMO+17 (16 %)	<sup>1</sup> MC
S <sub>88</sub>	47280	212	0.236	HOMO-8→LUMO+2 (17 %) HOMO-2→LUMO+9 (16 %)	<sup>1</sup> LC
S <sub>89</sub>	47402	211	0.0295	HOMO-9→LUMO (27 %) HOMO-6→LUMO+3 (16 %)	<sup>1</sup> LC
S <sub>91</sub>	47614	210	0.0663	HOMO-6→LUMO+4 (48 %)	<sup>1</sup> LC/ <sup>1</sup> ILCT

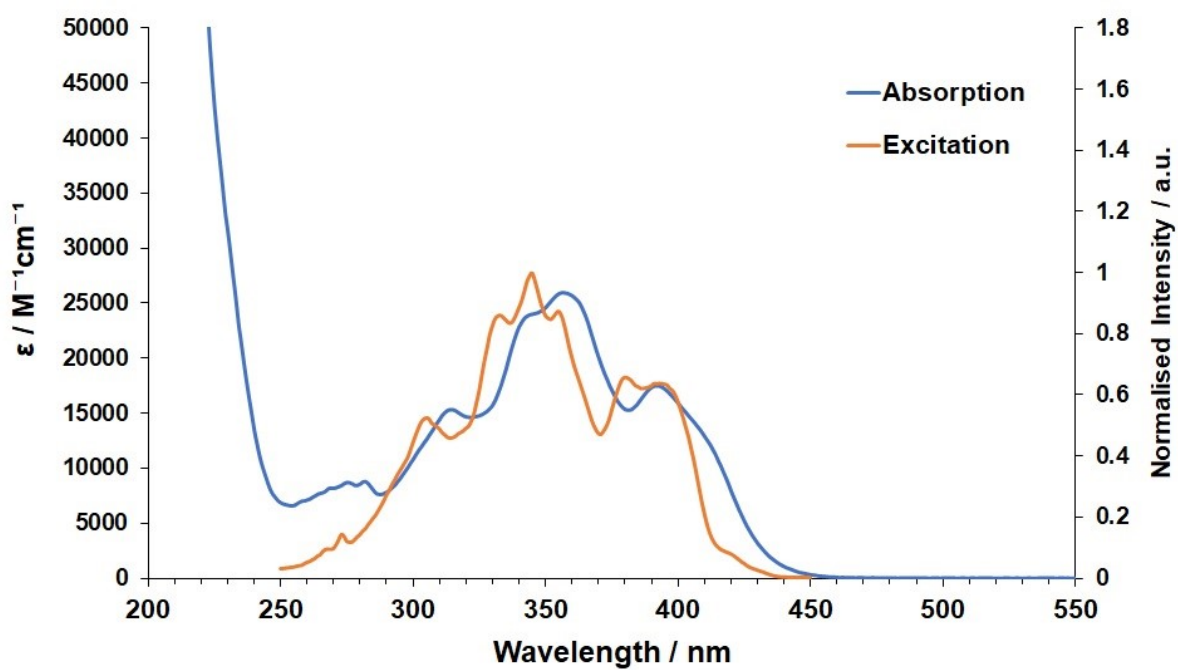
S <sub>92</sub>	47921	209	0.0795	HOMO-8→LUMO+2 (24 %) HOMO-7→LUMO+3 (17 %) HOMO-6→LUMO+4 (14 %) HOMO-6→LUMO+2 (12 %) HOMO-6→LUMO+5 (16 %)	<sup>1</sup> LC
S <sub>94</sub>	48102	208	0.0184	HOMO-7→LUMO+3 (22 %) HOMO-8→LUMO+3 (17 %)	<sup>1</sup> LC
S <sub>97</sub>	48324	207	0.0311	HOMO-7→LUMO+3 (16 %) HOMO-7→LUMO+3 (30 %) HOMO-8→LUMO+3 (20 %)	<sup>1</sup> LC
T <sub>1</sub>	26830	373		HOMO-1→LUMO (62 %) HOMO→LUMO+1 (13 %)	<sup>3</sup> MLCT (tz)
T <sub>2</sub>	27215	367		HOMO→LUMO+1 (39 %) HOMO→LUMO (29 %)	<sup>3</sup> MLCT (tz)
T <sub>3</sub>	27171	368		HOMO-1→LUMO+1 (21 %) HOMO→LUMO (35 %) HOMO→LUMO+1 (25 %)	<sup>3</sup> MLCT (tz)
T <sub>4</sub>	27418	365		HOMO-1→LUMO (13 %) HOMO-1→LUMO+2 (32 %)	<sup>3</sup> MLCT (tz)
T <sub>5</sub>	28874	346		HOMO→LUMO+4 (22 %) HOMO→LUMO+3 (12 %) HOMO-1→LUMO+1 (10 %)	<sup>3</sup> MLCT (tz)

**Table S3.** Selected TDDFT transitions for **Os** and their dominant composition and character.

State	Energy / cm <sup>-1</sup>	$\lambda$ / nm	$f(\text{osc})$	Composition	Character
S <sub>1</sub>	26047	384	0.00783	HOMO→LUMO (73 %)	<sup>1</sup> MLCT (tz)
S <sub>2</sub>	26839	373	0.0285	HOMO-1→LUMO+1 (21 %)	<sup>1</sup> MLCT (tz)
				HOMO-1→LUMO (24 %)	
S <sub>3</sub>	27331	366	0.0847	HOMO→LUMO+1 (18 %)	<sup>1</sup> MLCT (tz)
				HOMO-1→LUMO (34 %)	
				HOMO-1→LUMO+1 (24 %)	
				HOMO→LUMO (13 %)	
S <sub>4</sub>	29058	344	0.278	HOMO→LUMO+1 (20 %)	<sup>1</sup> MLCT (tz)
				HOMO-1→LUMO (23 %)	
S <sub>5</sub>	29545	339	0.129	HOMO→LUMO+3 (22 %)	<sup>1</sup> MLCT (tz)
				HOMO→LUMO+2 (21 %)	
				HOMO→LUMO+1 (20 %)	
S <sub>6</sub>	30199	331	0.0704	HOMO-1→LUMO+2 (29 %)	<sup>1</sup> MLCT (tz)
				HOMO→LUMO+2 (21 %)	
				HOMO→LUMO+4 (17 %)	
				HOMO-1→LUMO+3 (21 %)	
S <sub>7</sub>	30252	331	0.119	HOMO→LUMO+3 (29 %)	<sup>1</sup> MLCT (tz)
				HOMO-1→LUMO+3 (22 %)	
				HOMO→LUMO+2 (14 %)	
S <sub>8</sub>	30410	329	0.0396	HOMO-1→LUMO+4 (43 %)	<sup>1</sup> MLCT (tz)
				HOMO→LUMO+2 (16 %)	
				HOMO-1→LUMO+2 (14 %)	
S <sub>9</sub>	30698	326	0.0132	HOMO-2→LUMO (82 %)	<sup>1</sup> MLCT (tz)
S <sub>10</sub>	30879	324	0.139	HOMO-1→LUMO+2 (30 %)	<sup>1</sup> MLCT (tz)
				HOMO-1→LUMO+2 (24 %)	
				HOMO-1→LUMO+4 (23 %)	
S <sub>17</sub>	34861	287	0.0197	HOMO→LUMO+6 (76 %)	<sup>1</sup> MLCT (An)
S <sub>18</sub>	34924	286	0.0188	HOMO-1→LUMO+6 (87 %)	<sup>1</sup> MLCT (An)
S <sub>23</sub>	36026	278	0.0717	HOMO-1→LUMO+8 (60 %)	<sup>1</sup> MLCT (An + tz)
				HOMO-1→LUMO+10 (24 %)	
S <sub>29</sub>	37072	270	0.0178	HOMO-3→LUMO (53 %)	<sup>1</sup> ILCT (An→tz)
				HOMO-4→LUMO (10 %)	
S <sub>35</sub>	38034	263	0.0177	HOMO→LUMO+13 (31 %)	<sup>1</sup> MLCT (tz)
				HOMO→LUMO+12 (24 %)	
				HOMO-1→LUMO+12 (20 %)	
				HOMO→LUMO+11 (15 %)	
S <sub>36</sub>	38150	262	0.069	HOMO-1→LUMO+13 (31 %)	<sup>1</sup> MLCT (tz)
				HOMO→LUMO+11 (29 %)	
				HOMO-1→LUMO+12 (18 %)	
				HOMO-1→LUMO+11 (11 %)	
				HOMO→LUMO+13 (43 %)	
S <sub>37</sub>	38226	262	0.0215	HOMO→LUMO+13 (19 %)	<sup>1</sup> MLCT (tz)
				HOMO-1→LUMO+13 (43 %)	
S <sub>42</sub>	40439	247	0.0119	HOMO-3→LUMO+2 (54 %)	<sup>1</sup> ILCT (An→tz)
				HOMO-3→LUMO+3 (15 %)	
				HOMO-4→LUMO+2 (15 %)	
S <sub>58</sub>	43427	230	0.0105	HOMO-5→LUMO (71 %)	<sup>1</sup> ILCT (An→tz)
S <sub>62</sub>	43893	228	0.0122	HOMO-5→LUMO+1 (75 %)	<sup>1</sup> ILCT (An→tz)
				HOMO-7→LUMO+1 (14 %)	
S <sub>77</sub>	46444	215	0.0147	HOMO-5→LUMO+3 (54 %)	<sup>1</sup> ILCT (An→tz)
S <sub>79</sub>	46707	214	0.0536		<sup>1</sup> LC
				HOMO-4→LUMO+11 (24 %)	<sup>1</sup> ILCT (An→tz)

S <sub>81</sub>	46843	214	0.0625	HOMO-4→LUMO+8 (18 %) HOMO-3→LUMO+11 (15 %) HOMO-6→LUMO+3 (24 %) HOMO-3→LUMO+8 (20 %) HOMO-3→LUMO+10 (12 %)	<sup>1</sup> LC
S <sub>82</sub>	46887	213	0.033	HOMO-6→LUMO+2 (45 %)	<sup>1</sup> LC
S <sub>83</sub>	46923	213	0.0336	HOMO-9→LUMO (51 %)	<sup>1</sup> LC
S <sub>84</sub>	47012	213	0.021	HOMO-3→LUMO+9 (15 %) HOMO-3→LUMO+11 (31 %) HOMO-3→LUMO+9 (22 %) HOMO-9→LUMO (12 %) HOMO-3→LUMO+13 (11 %)	<sup>1</sup> LC
S <sub>86</sub>	47332	211	0.0679	HOMO-7→LUMO+2 (18 %)	<sup>1</sup> LC
S <sub>87</sub>	47380	211	0.0435	HOMO→LUMO+18 (41 %)	<sup>1</sup> LC
S <sub>88</sub>	47420	211	0.0364	HOMO→LUMO+16 (45 %)	<sup>1</sup> LC
S <sub>89</sub>	47495	211	0.0873	HOMO→LUMO+18 (30 %) HOMO-1→LUMO+18 (24 %) HOMO-8→LUMO+2 (11 %)	<sup>1</sup> LC
S <sub>90</sub>	47536	210	0.0189	HOMO-1→LUMO+18 (35 %) HOMO→LUMO+16 (16 %) HOMO-8→LUMO+4 (16 %)	<sup>1</sup> LC
S <sub>92</sub>	47633	210	0.0122	HOMO-1→LUMO+16 (53 %) HOMO-10→LUMO (15 %) HOMO→LUMO+16 (12 %)	<sup>1</sup> LC
S <sub>93</sub>	47686	210	0.0164	HOMO-8→LUMO+3 (19 %) HOMO-11→LUMO (17 %) HOMO-7→LUMO+3 (10 %)	<sup>1</sup> LC
S <sub>94</sub>	47714	210	0.0135	HOMO-10→LUMO (58 %)	<sup>1</sup> LC
S <sub>96</sub>	47966	209	0.0225	HOMO-6→LUMO+4 (47 %)	<sup>1</sup> LC
T <sub>1</sub>	23802	420	-	HOMO-1→LUMO (70 %) HOMO→LUMO+1 (20 %)	<sup>3</sup> MLCT (tz)
T <sub>2</sub>	24062	416	-	HOMO→LUMO+1 (45 %) HOMO→LUMO (27 %) HOMO-1→LUMO+1 (17 %)	<sup>3</sup> MLCT (tz)
T <sub>3</sub>	24377	410	-	HOMO→LUMO (44 %) HOMO→LUMO+1 (26 %) HOMO-1→LUMO (16 %)	<sup>3</sup> MLCT (tz)
T <sub>4</sub>	25545	392	-	HOMO-1→LUMO+1 (60 %) HOMO→LUMO (20 %)	<sup>3</sup> MLCT (tz)
T <sub>5</sub>	26302	380	-	HOMO-1→LUMO+3 (23 %) HOMO→LUMO+4 (18 %) HOMO-1→LUMO+2 (11 %)	<sup>3</sup> MLCT (tz)





**Fig. S19.** Overlaid electronic absorption profile recorded for a room temperature MeCN solution of **Os** (blue) and excitation profile corresponding to luminescence at  $\lambda_{\text{max}} = 472$  nm, recorded in a 4:1 EtOH/MeOH solvent glass at 77 K (orange).