

Supporting Information for
Luminescent osmium(II) bi-1,2,3-triazol-4-yl complexes:
photophysical characterisation and application in light-
emitting electrochemical cells

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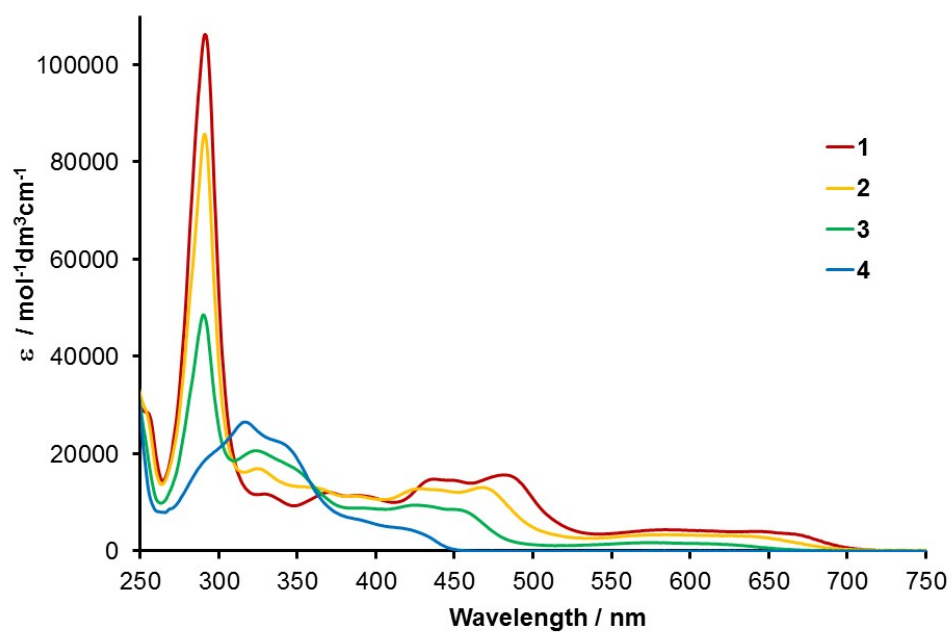


Figure S1: UV-Visible electronic absorption spectra for CH_2Cl_2 solutions of complexes **1-4**.

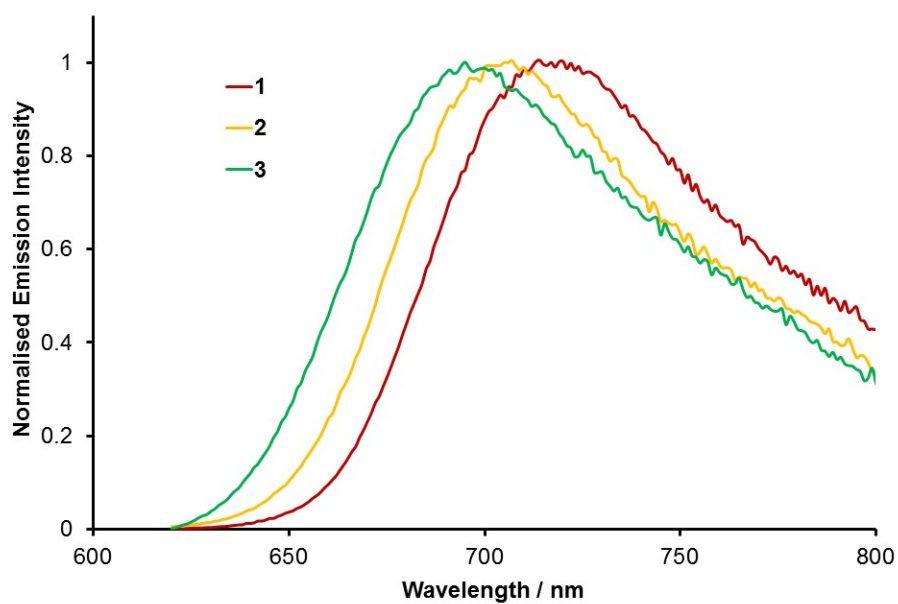
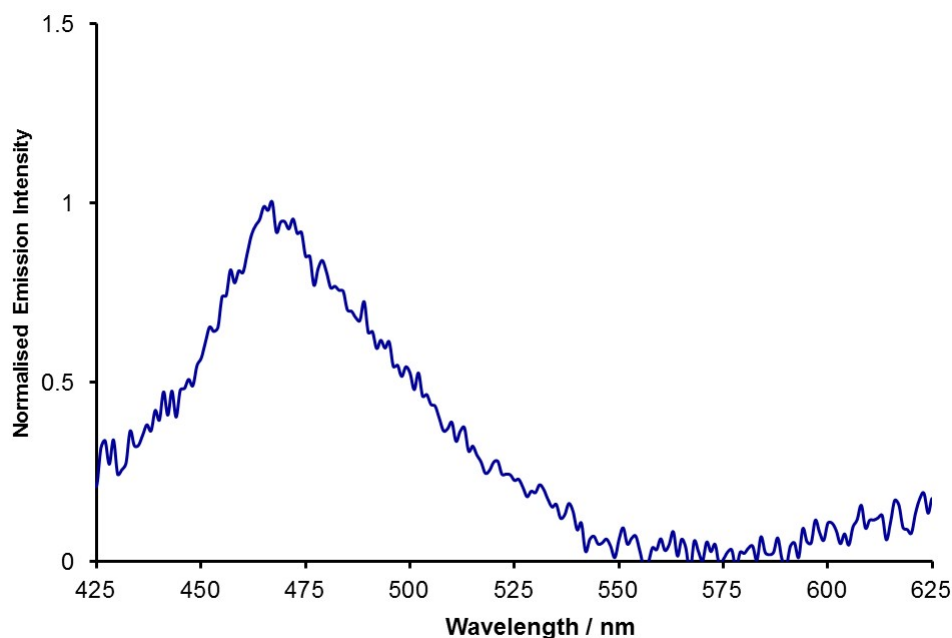


Figure S2: Normalised emission spectra recorded for aerated CH_2Cl_2 solutions of complexes **1-3** at room temperature.

Table S1: Summarised photophysical data for room temperature CH₂Cl₂ solutions of 1-4.

Complex	$\lambda_{\text{(abs)}}$ / nm	$\lambda_{\text{(em)}}$ / nm ^a	$\tau_{\text{(aerated)}}$ / ns	$\tau_{\text{(degassed)}}$ / ns	$\Phi_{\text{(aerated)}}$ / % ^b	$\Phi_{\text{(degassed)}}$ / % ^b
1	648, 585, 480, 449, 437, 390, 369, 329, 291	717	73	90	1.1	1.4
2	634, 578, 467, 438, 427, 387, 359, 325, 291	705	95	131	1.5	2.0
3	613, 568, 450, 425, 392, 324, 290	697	123	175	1.9	2.8
4	418, 388, 338, 316, 292	-	-	-	-	-

^a $\lambda^{\text{ex}} = 600$ nm; ^b Relative to [Ru(bpy)₃][PF₆]₂ $\Phi_{\text{em}} = 0.018$ in aerated MeCN

**Figure S3:** Normalised emission spectrum recorded for [Os(btz)₃][PF₆]₂ (**4**) in aerated MeCN at room temperature ($\lambda^{\text{ex}} = 365$ nm). Weak emission is discernible above the noise level after subtraction of solvent Raman scattering signals.

Current Data Parameters
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 EXPNO 10
 PROCNO 1

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 Date_ 20150921
 Time 12:36
 TIMEORIG 12:36
 PROGRAM 5 mm PABBO F2/
 PULPROG zg30
 TD 65536
 CD 32768
 NS 64
 DS 2
 SWH 8223.685 Hz
 FIDRES 3.9835883 Hz
 AQ 3.9835883 Hz
 RG 134.04
 DW 60.800 usec
 DE 19.69 usec
 TE 293.15 K
 D1 1.00000000 sec
 TD0 4

 CHANNEL f1
 SFO1 400.1324710 MHz
 NUC1 1H
 P1 8.00 usec
 PL1 24.00000000 W

 F2 - Processing parameters
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 SF 400.1300132 MHz
 WF 1.00000000 Hz
 SSB 0
 LB 0
 GB 0
 PC 1.50

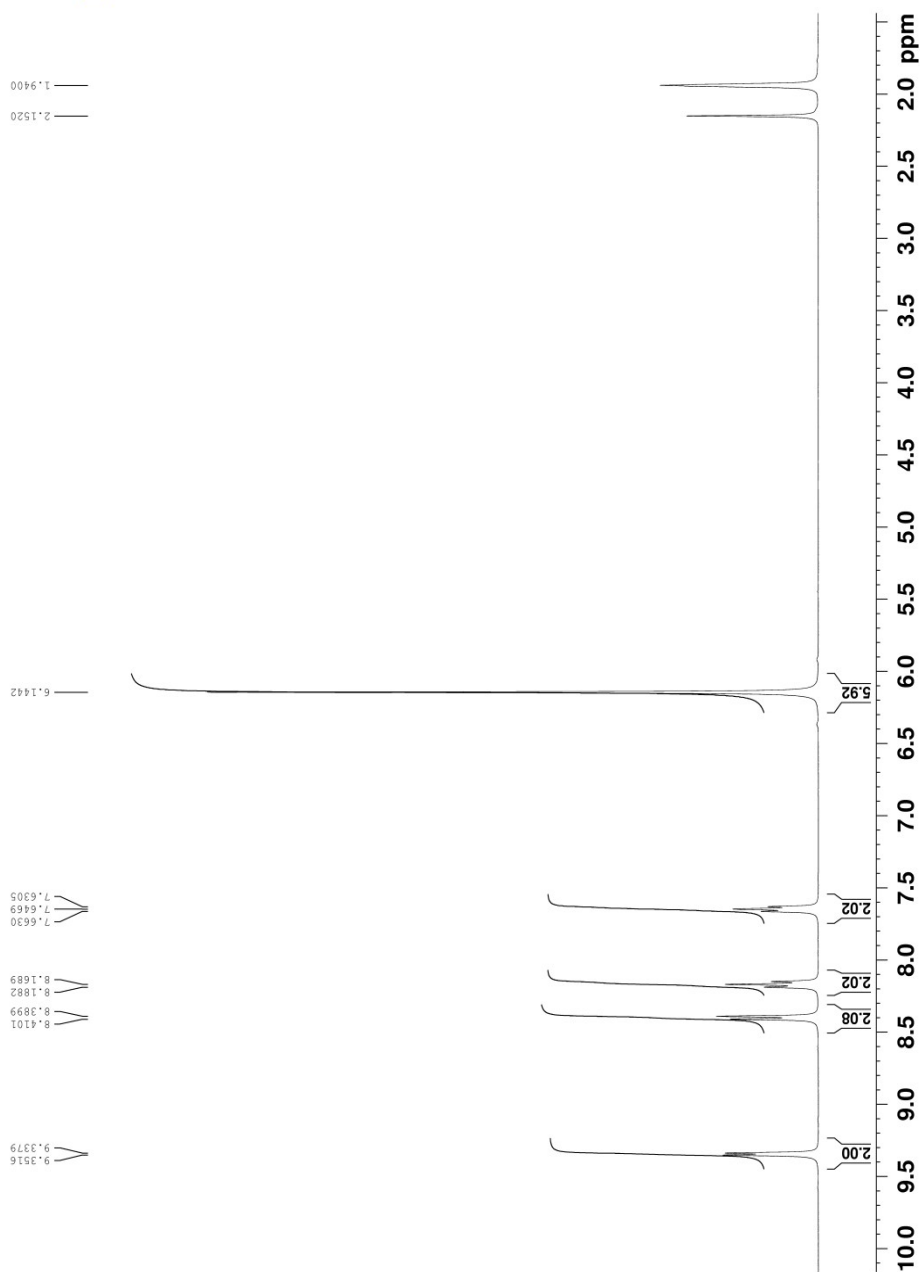


Figure S4: ¹H NMR (400 MHz, d₃-MeCN) of [Os(η⁶-C₆H₆)(bpy)Cl][PF₆]

```

Current Data Parameters
NAME      N6284
EXPNO    10
PROCNO   1

F2 - Acquisition Parameters
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Time     19.22
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PULPROG  zgpg30
TD       65536
SOLVENT  CD3CN
NS       256
DS       4
SWH      24038.461 Hz
FIDRES   0.366798 Hz
AQ       1.381195 sec
RG       381.72
DW       20.800 usec
DE       8.18 usec
TE       300.2 K
D1       2.00000000 sec
D11      0.03000000 sec
D10      0.03000000 sec
TD0      1

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NUC1     13C
P1       9.00 usec
PLM1     77.00000000 W

===== CHANNEL f2 =====
SFO2     400.1316005 MHz
NUC2     1H
P2       9.00 usec
PLM2     77.00000000 W
PCPD2    waltz16
PCPD2/2  90.00 usec
PLM2     24.00000000 W
PLM12    0.116229999 W
PLM13    0.116229999 W

F2 - Processing parameters
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SF       100.6228284 MHz
WDW      EM
SSB      0
LB       0.50 Hz
GB       0
PC       1.40
    
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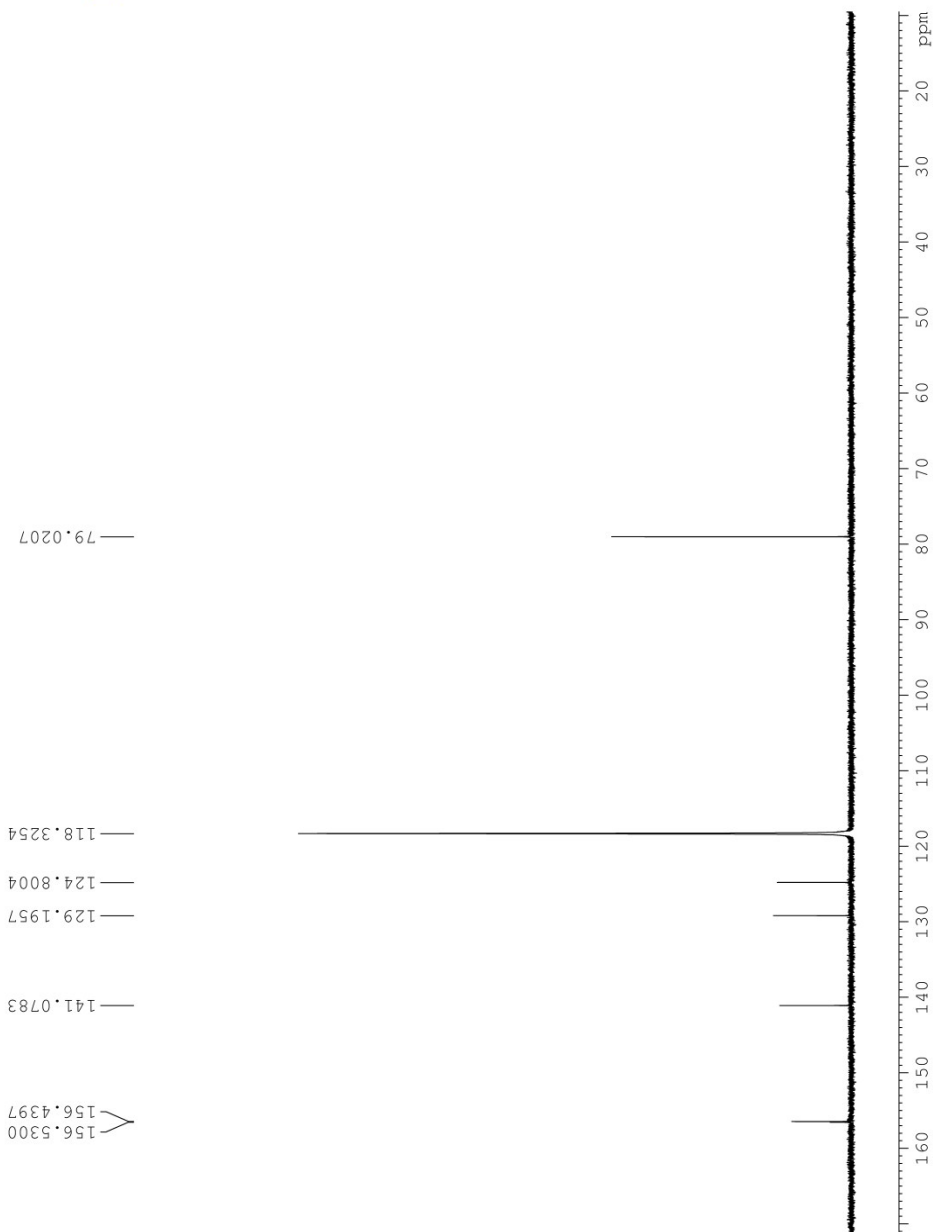


Figure S5: ^{13}C NMR (101 MHz, d_3 -MeCN) of $[\text{Os}(\eta^6\text{-C}_9\text{H}_9)(\text{bpy})\text{Cl}][\text{PF}_6]$

```

Current Data Parameters
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EXPNO    10
PROCNO   1

F2 - Acquisition Parameters
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INSTRUM  spect
PROBHD   5 mm PABBO
PULPROG  zg30
TD       65536
SOLVENT  CDCl3
DS       4
SWH      8223.685 Hz
FIDRES   0.125483 Hz
AQ       3.524788 sec
RG       317.88
RO       0.6288888
DE       60.800 usec
TE       10.69 usec
D1       2.0000000 sec
D2       1.0000000 sec
TD0      4

===== CHANNEL f1 =====
NUC1     13C
P1       8.00 usec
PL1      0.0000000 W
===== CHANNEL f2 =====
SI - Processing Parameters
SF       400.1300116 MHz
WDW      EM
SSB      0
LB       0.30 Hz
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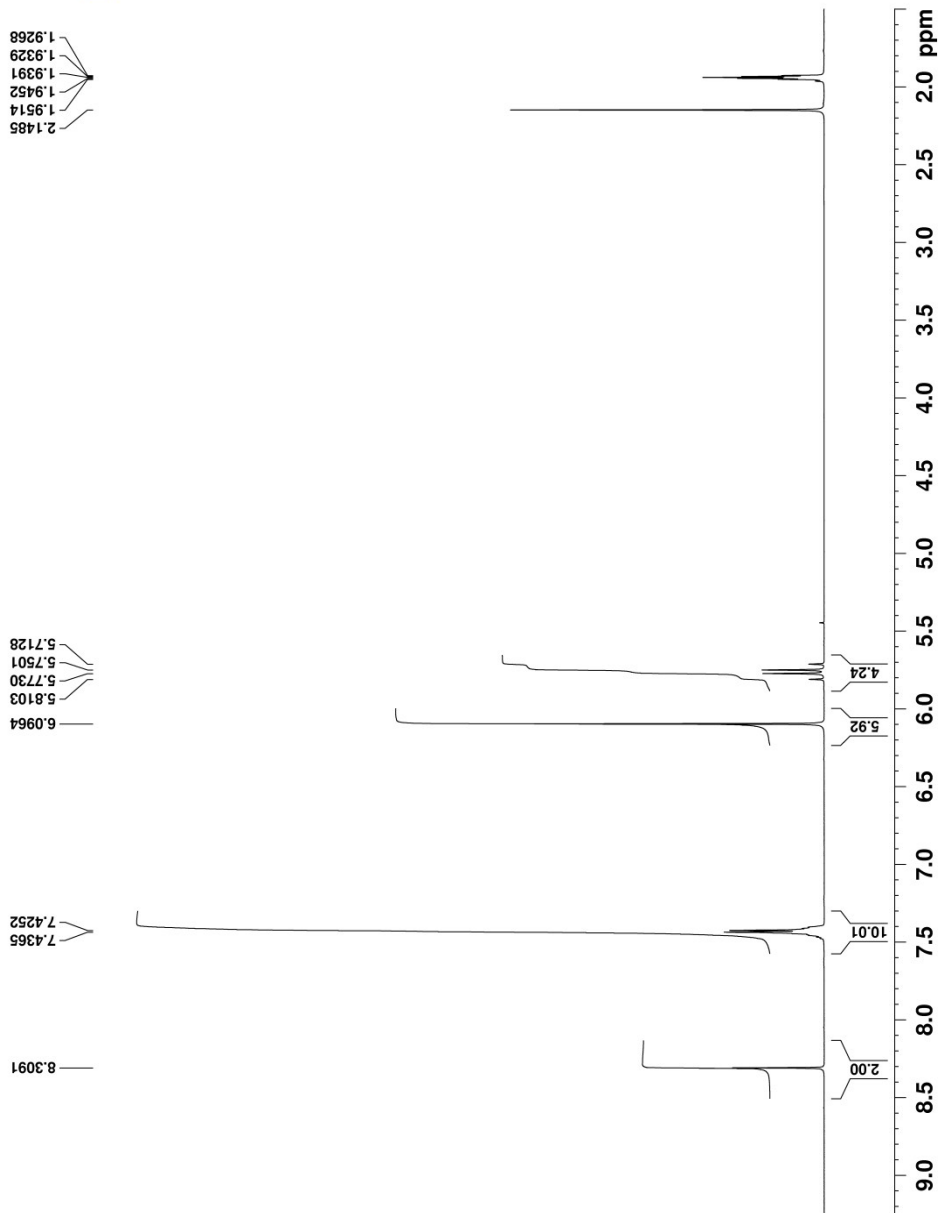


Figure S6: ¹H NMR (400 MHz, d₃-MeCN) of [Os(η⁶-C₆H₆)(btz)Cl][PF₆]

```

Current Data Parameters
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EXPNO    10
PROCNO   1

F2 - Acquisition Parameters
Date_    20151111
Time     7.55
INSTRUM  spect
PROBHD   5 mm PABBO
PULPROG  zgpg30
TD       65536
SOLVENT  CD3CN
NS       514
DS       4
SWH      24038.461 Hz
FIDRES  0.366798 Hz
AQ       1.381192 sec
RG       181.92
DM       20.800 usec
DE       8.18 usec
TE       300.2 K
D1       2.0000000 sec
D11      0.0300000 sec
TD0      1

===== CHANNEL F1 =====
SF01    100.6228303 MHz
NUC1     13C
P1       5.00 usec
PLM1    77.00000000 W

===== CHANNEL F2 =====
SF02    400.1316005 MHz
NUC2     1H
PCPDPRG12  waltz16
PCPD2     90.00 usec
PLM2     24.0000000 W
PLM12    0.1750000 W
PLM13    0.1422599 W

F2 - Processing parameters
SI       65536
SF       100.6126728 MHz
WDW      RM
SSB      0
LB       0
GB       0
PC       1.40
    
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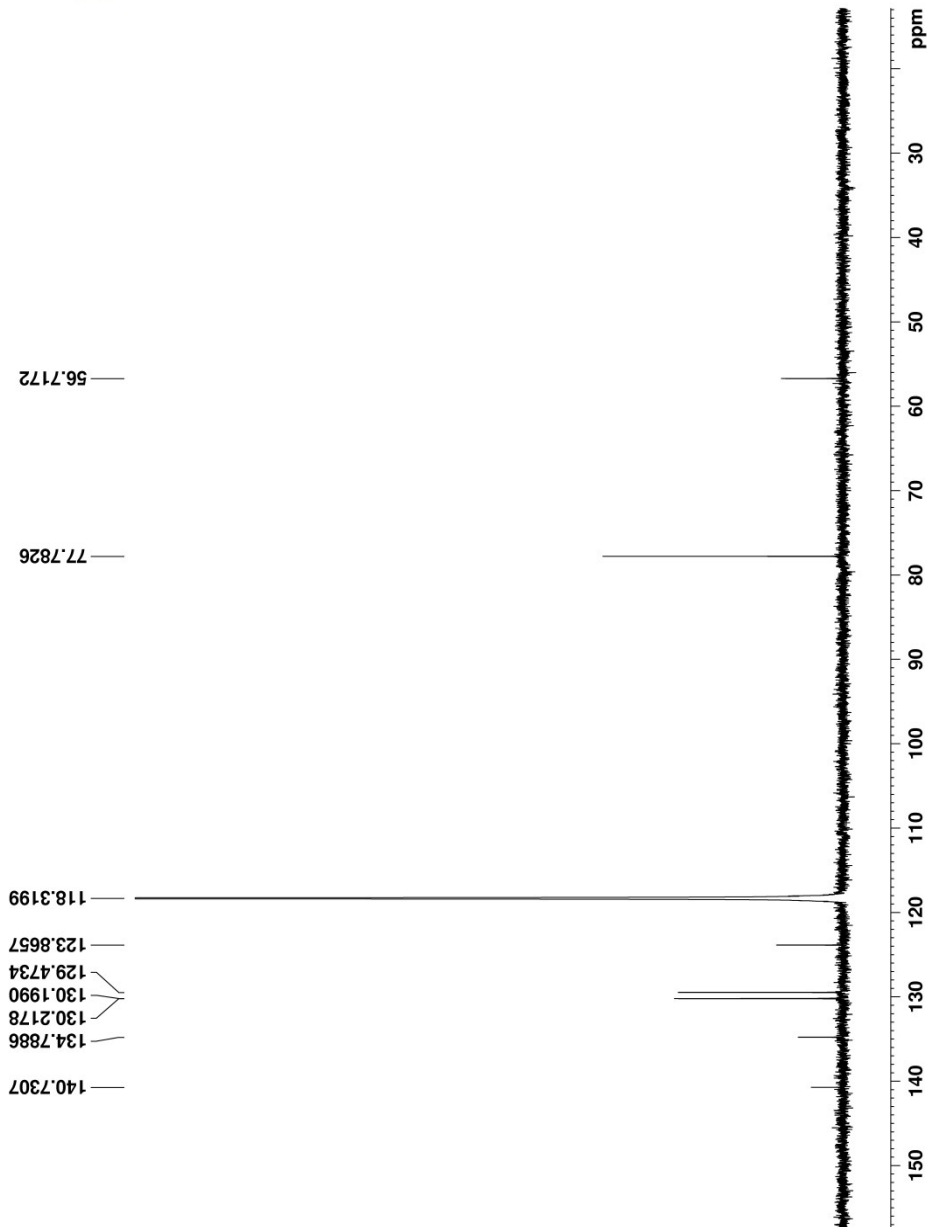


Figure S7: ¹³C NMR (101 MHz, d₃-MeCN) of [Os(η⁶-C₆H₆)(btz)Cl][PF₆]

Current Data Parameters
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 PROCNO: 1
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 INSTRUM: spect
 PULPROG: zgpg30
 FULPRAG: 65536
 ID: 1
 SOLVENT: CD3CN
 NS: 12
 DS: 2
 SWH: 8223.685 Hz
 FIDRES: 0.125483 Hz
 AQ: 0.29588 sec
 RG: 64.888 sec
 DW: 60.800 usec
 DE: 10.69 usec
 DI: 3.000000 K
 D1: 2.0000000 sec
 TD0: 1
 ===== CHANNEL f1 =====
 SFO1: 400.1524710 MHz
 NUC1: 1H
 P1: 8.00 usec
 PL1: 24.00000000 W
 FLM1:
 F2 - Processing parameters
 SI: 32768
 SF: 400.1300115 MHz
 Mode: EM
 SSB: 0
 LB: 0.30 Hz
 GB: 0
 PC: 1.50

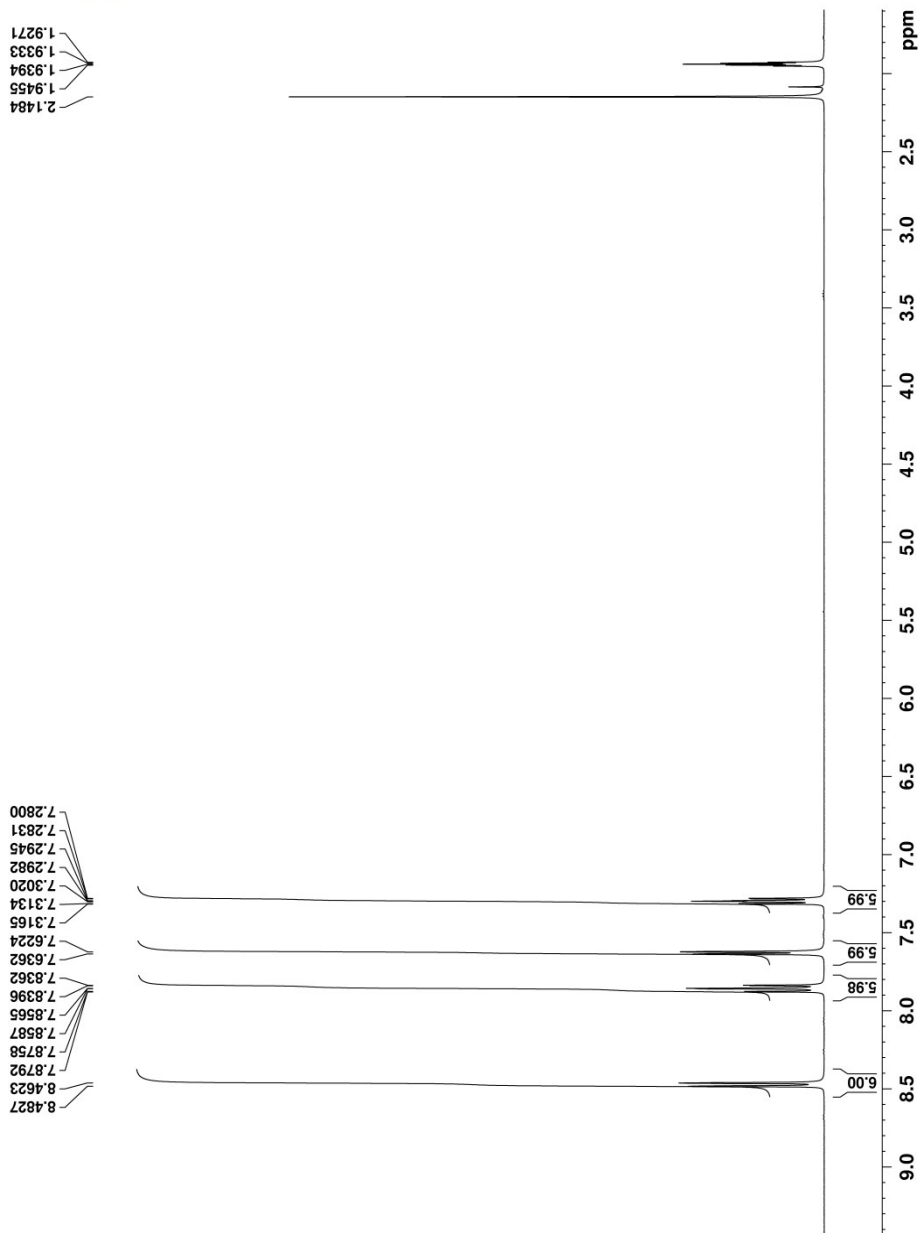


Figure S8: ¹H NMR (400 MHz, d₃-MeCN) of [Os(bpy)₃][PF₆]₂ (Complex 1)



Figure S9: ^{13}C NMR (101 MHz, d_3 -MeCN) of $[\text{Os}(\text{bpy})_3][\text{PF}_6]_2$ (Complex 1)

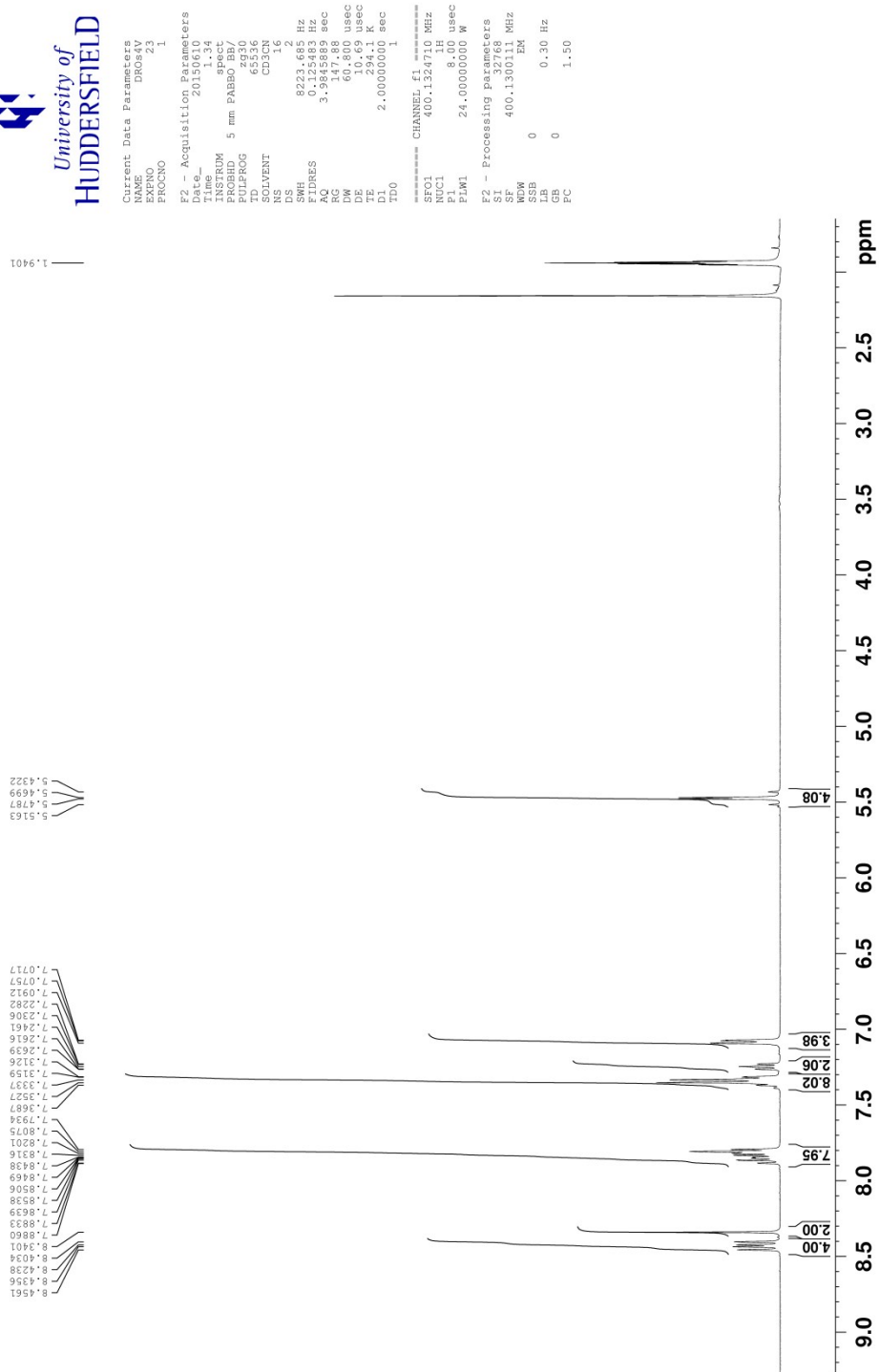


Figure S10: ^1H NMR (400 MHz, $\text{d}_3\text{-MeCN}$) of $[\text{Os}(\text{bpy})_2(\text{btz})][\text{PF}_6]_2$ (Complex 2)



Figure S11: ^{13}C NMR (101 MHz, d_3 -MeCN) of $[\text{Os}(\text{bpy})_2(\text{btz})][\text{PF}_6]_2$ (Complex 2)

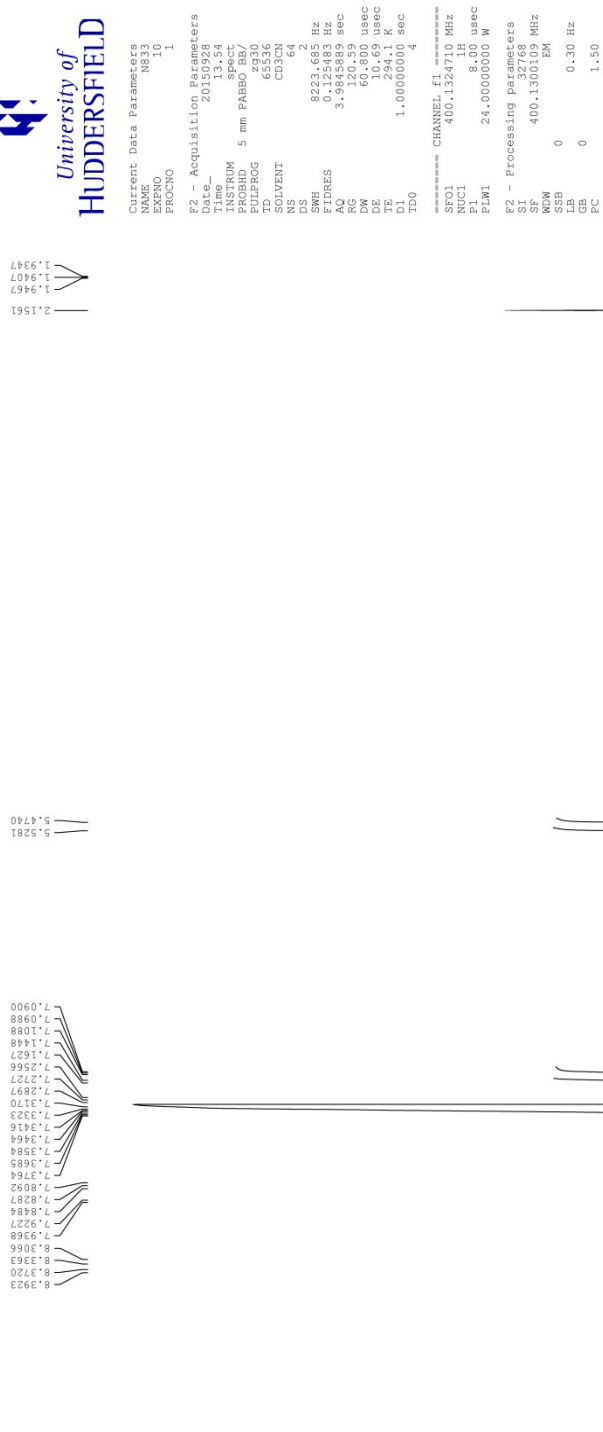


Figure S12: ^1H NMR (400 MHz, d_3 -MeCN) of $[\text{Os}(\text{bpy})(\text{btz})_2][\text{PF}_6]_2$ (Complex 3)

```

Current Data Parameters
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PROCNO 1
F2 - Acquisition Parameters
Date_ 20150928
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PULPROG zgpg30
TD 65536
SOLVENT CD3CN
DS 5
NS 514
SWH 24038.461 Hz
FIDRES 0.366788 Hz
AQ 1.353149 sec
RG 327.5
DW 20.800 usec
DE 8.18 usec
TE 294.4 K
D1 0.0300000 sec
D11 0.0300000 sec
DPO 1
===== CHANNEL f1 =====
SFO1 100.6228284 MHz
NUC1 13C
P1 9.00 usec
PWL1 77.00000000 W
===== CHANNEL f2 =====
SFO2 400.1316005 MHz
NUC2 1H
P2 12.00 usec
PWL2 1.00000000 W
===== CHANNEL f3 =====
SFO3 400.1316005 MHz
NUC3 1H
P3 12.00 usec
PWL3 1.00000000 W
F2 - Processing parameters
SI 65536
SF 100.6126624 MHz
WDW EM
SSB 0
LB 0.50 Hz
GB 0
FC 1.40
    
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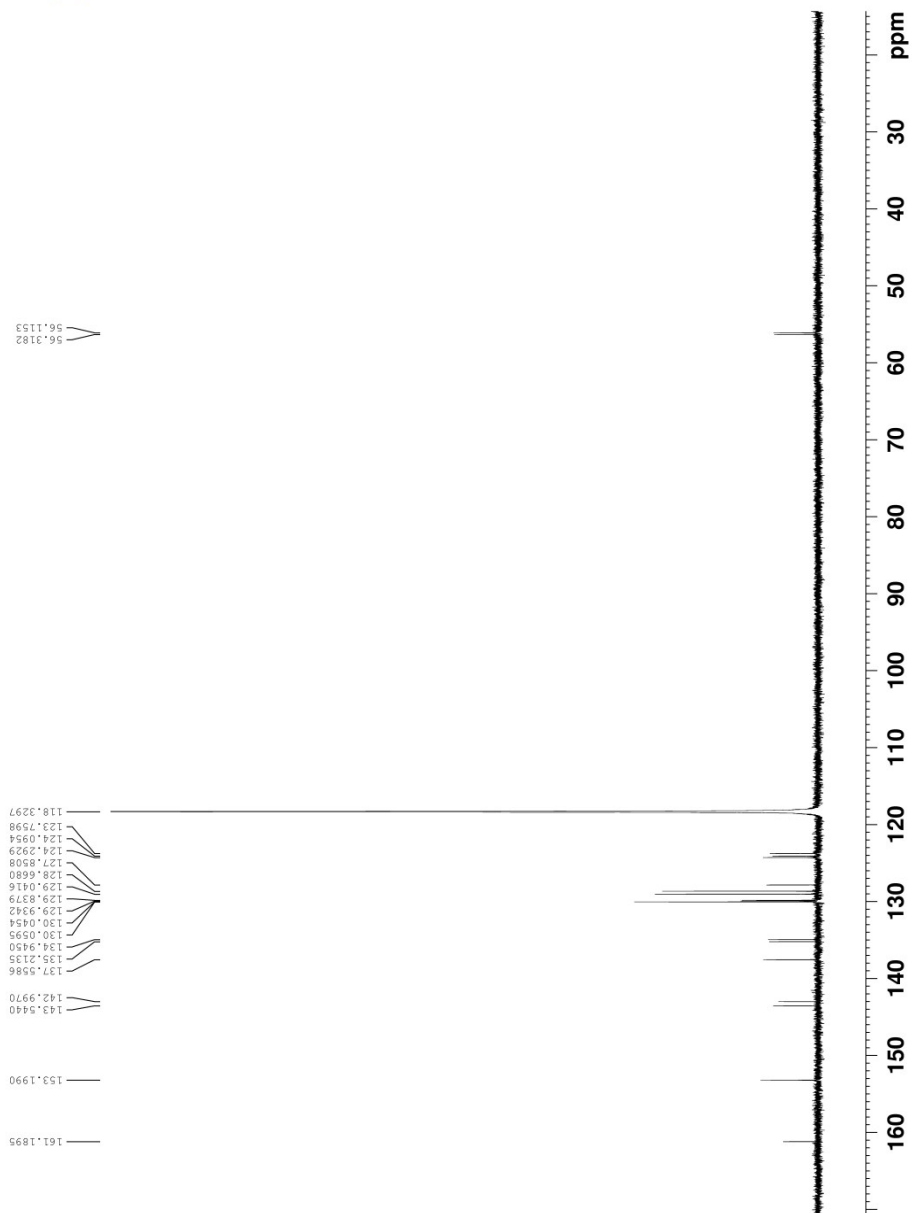


Figure S13: ¹³C NMR (101 MHz, d₃-MeCN) of [Os(bpy)(btz)₂][PF₆]₂ (Complex 3)

Current Data Parameters
 NAME 0860
 EXPNO 10
 PROCNO 1

 F2 - Acquisition Parameters
 Date_ 20151123
 Time 16.25
 INSTRUM spect
 PULPROG zgpg30
 TD 65536
 SOLVENT CD3CN
 DS 4
 SMH 8223.685 Hz
 FIDRES 0.125483 Hz
 AQ 3.29833 sec
 RG 1024.33
 DW 60.800 usec
 DE 10.69 usec
 TE 298.15 K
 D1 1.00000000 sec
 TP0 4

 ===== CHANNEL f1 =====
 ST01 400.1324710 MHz
 NUC1 1H
 P1 8.00 usec
 PLW1 24.00000000 W

 F2 - Processing parameters
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 SF 400.1300112 MHz
 SSF 0
 SSB 0
 LB 0.30 Hz
 GB 0
 FC 1.50

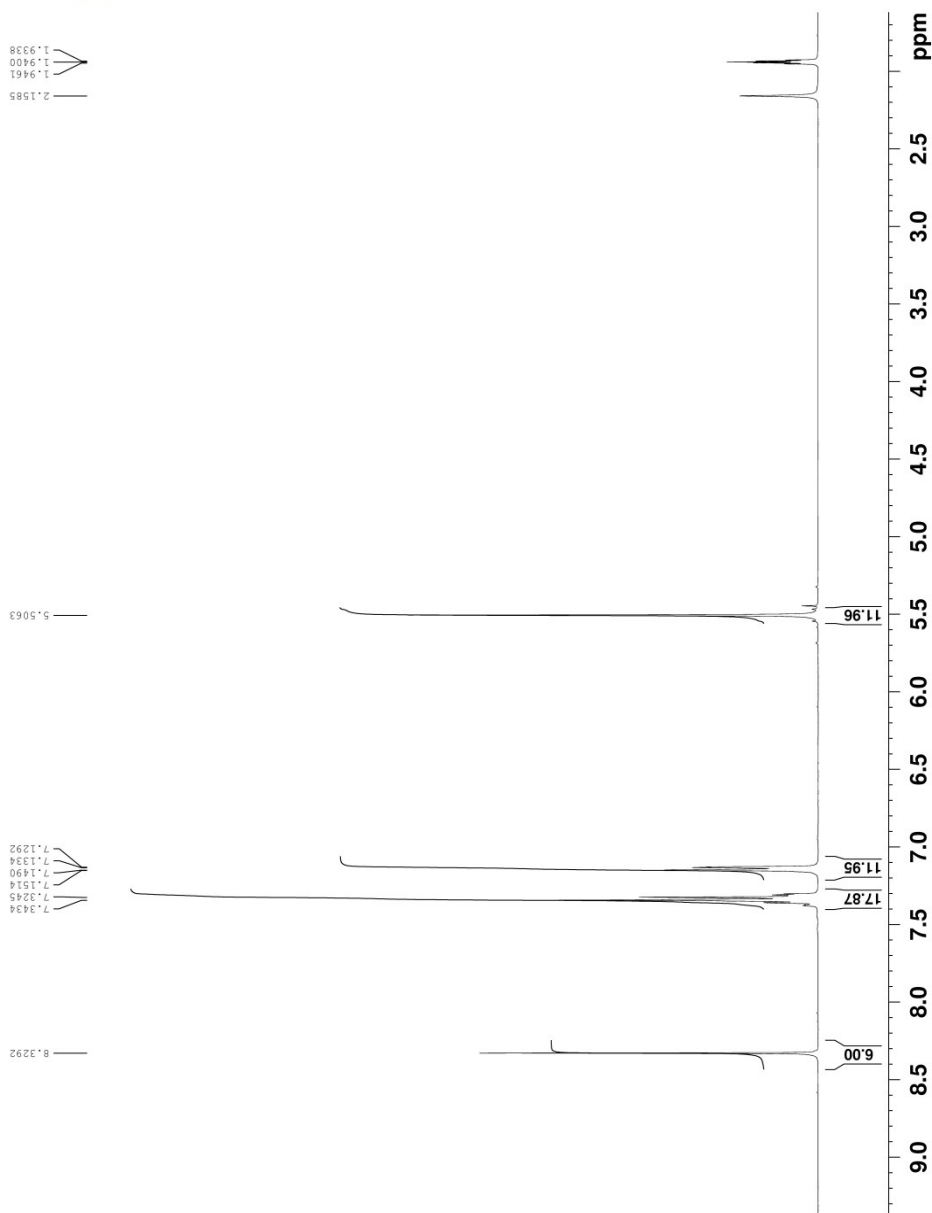


Figure S14: ¹H NMR (400 MHz, d₃-MeCN) of [Os(btz)₃][PF₆]₂ (Complex 4)

```

Current Data Parameters
NAME      4861
EXPNO    10
PROCNO   1

F2 - Acquisition Parameters
Date_    20151123
Time     17.08
INSTRUM  spect
PROBHD   5 mm PABBO-7
PULPROG  zgpg30
TD        65536
SOLVENT  CD3CN
DS        2
SI        4
SWH       24038.461 Hz
FIDRES    0.3667798 Hz
AQ         1.3814929 sec
RG         381.72
DE         20.800 usec
DELTA     8.18 usec
TE        300.2 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0        1

===== CHANNEL F1 =====
SFO1      100.6228303 MHz
NUC1      13C
P1         9.00 usec
PL1       77.00000000 W

===== CHANNEL F2 =====
SFO2      400.1316005 MHz
NUC2      13C
P2         9.00 usec
PL2       77.00000000 W
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PCPD2     waltz16
PCPD1     waltz16
PCPD2/2   90.00 usec
PLW2      24.00000000 W
PLW1      0.17250000 W
PLW1/2    0.14229999 W

F2 - Processing parameters
SI         65536
SF         100.6228303 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
    
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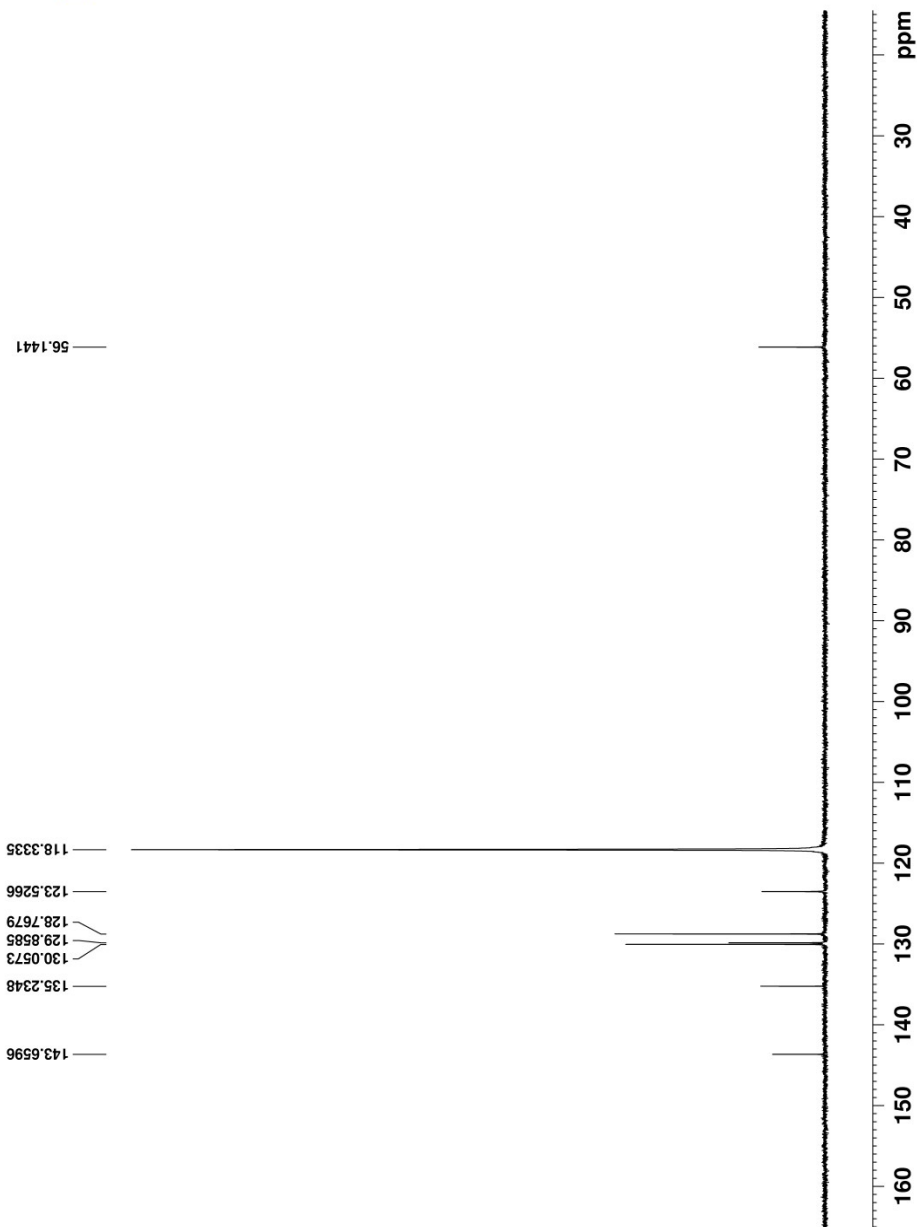


Figure S15: ¹³C NMR (101 MHz, *d*₃-MeCN) of [Os(btz)₃][PF₆]₂ (Complex 4)

Optimised ground state geometry of the dication [Os(bpy)]²⁺ (Complex 1)

61

geometry

C	-0.43206863	4.12929253	-1.19301751
C	0.39846474	4.31586787	-2.28954884
C	1.13802543	3.23367231	-2.75940923
C	1.01952871	2.01232390	-2.11580824
N	0.21440503	1.81875589	-1.05005516
C	-0.51351054	2.87583239	-0.58371466
C	-1.36652433	2.58306558	0.57910558
N	-1.28889403	1.30285576	1.04792002
C	-2.04307580	0.96127670	2.11378176
C	-2.88935204	1.85147883	2.75512098
C	-2.97325861	3.15864878	2.28275443
C	-2.20337631	3.52132615	1.18606714
N	1.46711677	-1.09965440	-1.04752256
C	1.23006240	-1.89895263	-2.10886326
C	2.22725792	-2.61537609	-2.75096911
C	3.53519795	-2.51361978	-2.28427156
C	3.79108031	-1.69563042	-1.19230148
C	2.74747889	-0.99540947	-0.58432331
C	2.92275479	-0.10452308	0.57373347
C	4.15494806	0.15415822	1.17691453
C	4.22795838	1.00763960	2.26925985
C	3.05487512	1.59076836	2.74117456
C	1.85951916	1.29972998	2.10369412
N	1.77615885	0.47059290	1.04204397
Os	0.00081754	-0.00009026	0.00066698
N	-1.68680001	-0.72542405	-1.04034037
C	-2.23573366	-1.88399261	-0.57008407
C	-1.54925463	-2.47549682	0.58938268
C	-1.93981396	-3.66906946	1.19921464
C	-1.23471449	-4.15363314	2.29237920
C	-0.14226264	-3.42683315	2.75839475
C	0.20178726	-2.24916826	2.11443705
N	-0.47696970	-1.76767498	1.05190758
C	-2.26286252	-0.12576737	-2.10339230
C	-3.38342239	-0.63423872	-2.74038038
C	-3.94831665	-1.81539765	-2.26644702
C	-3.36539815	-2.44057830	-1.17267718
H	-1.01218711	4.96000267	-0.81382707
H	0.46707350	5.28637970	-2.76666009
H	1.80031887	3.32818204	-3.61124894
H	1.57593716	1.14758791	-2.45142402
H	-1.94880680	-0.06201884	2.45138710
H	-3.46983669	1.51946926	3.60717897
H	-3.62557346	3.88170343	2.75805888
H	-2.25800568	4.53234241	0.80492871
H	0.20229587	-1.95011071	-2.44214287
H	1.97625944	-3.24040528	-3.59922295
H	4.34043424	-3.06061462	-2.76032430
H	4.80132763	-1.60666059	-0.81561815
H	5.05708604	-0.30585467	0.79620551
H	5.18125000	1.21345156	2.74160722
H	3.05926766	2.26365559	3.58993826
H	0.92682174	1.73126917	2.44110398
H	-2.78998954	-4.22231995	0.82302426

H	-1.53192743	-5.07986814	2.76986117
H	0.44018776	-3.76287523	3.60752478
H	1.04250565	-1.65543910	2.44711529
H	-1.79397641	0.78814541	-2.44235632
H	-3.80110989	-0.10856122	-3.59031890
H	-4.82579768	-2.24152670	-2.73833367
H	-3.79270369	-3.35800133	-0.79038426

Optimised ground state geometry of the dication [Os(bpy)₂(btz)]²⁺ (Complex 2)

61

geometry

C	3.42150948	-3.04135894	-1.86041416
C	2.76498902	-3.29962717	-0.66504864
C	1.83042104	-2.38854153	-0.17188577
N	1.54340025	-1.23957671	-0.84909976
C	2.18752794	-0.99790963	-2.00783430
C	3.12604814	-1.86532984	-2.54331888
C	1.25774844	-3.67072572	1.93411630
C	0.53407553	-3.75134288	3.11574567
C	-0.34567216	-2.71947612	3.43328803
C	-0.47084086	-1.65457176	2.55590453
N	0.22432267	-1.56858753	1.40269175
C	1.09358547	-2.57250385	1.08791401
C	0.46847162	3.75831096	-3.11628899
C	1.19528491	3.68915894	-1.93586379
C	1.05038428	2.58819019	-1.08970650
N	0.19701987	1.57037100	-1.40334013
C	-0.50116811	1.64525519	-2.55553500
C	-0.39475959	2.71228043	-3.43279891
C	2.71281352	3.34186381	0.66058852
C	3.37549848	3.09402278	1.85476678
C	3.10032696	1.91322426	2.53790123
C	2.17506893	1.03081606	2.00382902
N	1.52505996	1.26226007	0.84628788
C	1.79225286	2.41587236	0.16882855
N	-1.67680336	-2.00556807	-1.67666873
N	-2.98337696	-2.23468837	-1.84322467
C	-3.74160681	-1.38134655	-1.11314393
C	-2.83558189	-0.57588855	-0.46103398
N	-1.58168480	-1.00041188	-0.84352945
N	-1.70612674	1.98494323	1.67016271
N	-3.01571955	2.20552381	1.82397163
C	-3.76142566	1.33565173	1.10032350
C	-2.84382600	0.53315215	0.46106080
N	-1.59627055	0.97425611	0.84569277
C	-3.42808868	-3.34369345	-2.69158814
C	-3.47847299	3.26553079	2.72391702
Os	0.07374002	-0.00022847	-0.00023120
H	4.14922299	-3.74372385	-2.24944607
H	2.98285247	-4.20844122	-0.12013184
H	1.92761930	-0.07694023	-2.51122866
H	3.61185493	-1.61691728	-3.47891935
H	1.94981437	-4.46086494	1.67520729
H	0.65761496	-4.60073012	3.77727306
H	-0.92769993	-2.73343013	4.34667041
H	-1.13665984	-0.82835154	2.76670163
H	0.57703243	4.60981804	-3.77771265
H	1.87481736	4.49039044	-1.67784359

H	-1.15364738	0.80830081	-2.76574741
H	-0.97838177	2.71694550	-4.34525155
H	2.91501169	4.25417181	0.11546763
H	4.09242782	3.80799655	2.24268932
H	3.59169797	1.67253158	3.47260913
H	1.93103567	0.10565447	2.50747822
H	-4.81878433	-1.41651470	-1.11560236
H	-4.83893556	1.36003411	1.09679985
H	-4.31107037	-3.03762833	-3.24989440
H	-3.65857507	-4.21392194	-2.07675641
H	-2.62148618	-3.58176352	-3.38003719
H	-4.26008358	3.84271228	2.23232189
H	-2.62902278	3.90720757	2.94206779
H	-3.86029769	2.83095286	3.64781736

Optimised ground state geometry of the dication [Os(bpy)(btz)₂]²⁺ (Complex 3)

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geometry

C	-0.44174366	3.99580670	2.86488723
C	-0.23383429	4.09262186	1.49596826
C	-0.13464499	2.93537900	0.72308171
N	-0.23996533	1.70091633	1.29217686
C	-0.43246925	1.61674744	2.62264334
C	-0.54036862	2.73145696	3.43841338
C	0.18271455	4.09047386	-1.50569006
C	0.39192466	3.99193529	-2.87428893
C	0.50672868	2.72711620	-3.44375730
C	0.41301727	1.61374016	-2.62442117
N	0.21935971	1.69970655	-1.29423825
C	0.09826555	2.93454025	-0.72910003
N	-0.08850271	-2.19420263	-2.19845925
N	0.80449468	-3.00917761	-2.77002606
C	2.05391619	-2.80642158	-2.28515368
C	1.91261928	-1.79867216	-1.35889426
N	0.57783868	-1.45677093	-1.34651284
N	2.89941702	0.54288061	1.06989935
N	4.10594542	0.01063572	0.85298228
C	4.06434793	-0.96786573	-0.08341030
C	2.74235898	-1.03772130	-0.45830581
N	2.07172189	-0.09099762	0.28227321
C	0.36486666	-3.99952163	-3.75499496
C	5.27463041	0.54496817	1.55483253
N	0.11734309	-2.18592945	2.20881568
N	-0.76521766	-3.01048750	2.78285933
C	-2.01710180	-2.82514252	2.29734769
C	-1.88859145	-1.81855859	1.36797617
N	-0.55827577	-1.45971121	1.35456066
N	-2.90495941	0.50235872	-1.06841159
N	-4.10460570	-0.04460402	-0.84990264
C	-4.05060581	-1.01946009	0.08964983
C	-2.72788219	-1.07116334	0.46489878
N	-2.06932746	-0.11832366	-0.27866072
C	-0.31329998	-3.99149233	3.77161977
C	-5.27993921	0.47250822	-1.55355181
Os	0.00011756	0.06370424	0.00157611
H	-0.51960571	4.89006911	3.47201095
H	-0.14431530	5.06705018	1.03459881
H	-0.48806764	0.61591955	3.02848739

H	-0.69448650	2.60365915	4.50283279
H	0.08074012	5.06515463	-1.04744763
H	0.45839915	4.88516962	-3.48427385
H	0.66254331	2.59788571	-4.50775695
H	0.48141753	0.61240885	-3.02705582
H	2.90603185	-3.37187722	-2.62504290
H	4.94185840	-1.51142680	-0.39274668
H	1.08265959	-4.03933488	-4.57268893
H	-0.60459037	-3.68525901	-4.13260998
H	0.27926081	-4.98047100	-3.28697072
H	5.77228030	1.29284513	0.93701809
H	5.96108367	-0.26964032	1.77851075
H	4.93084926	1.00016917	2.48002813
H	-2.86196214	-3.40035758	2.63897739
H	-4.92112087	-1.57322299	0.40064720
H	-1.02533511	-4.03020314	4.59442195
H	0.65668778	-3.66867866	4.14052308
H	-0.22471200	-4.97501818	3.30961580
H	-5.95712055	-0.35116788	-1.77219865
H	-4.94228302	0.92667730	-2.48151248
H	-5.78567277	1.21787874	-0.93928179

Optimised ground state geometry of the dication [Os(btz)₃]²⁺ (Complex 4)

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geometry

N	2.34852699	0.06761760	2.06707449
N	3.42931777	0.82791492	2.26737225
C	3.54944825	1.79254126	1.32243967
C	2.46702808	1.60792597	0.49434203
N	1.76142441	0.53957297	0.99993444
N	0.27632095	2.23126785	-2.18300546
N	1.16203112	3.19122185	-2.46635645
C	2.17814629	3.22052897	-1.56942455
C	1.89222419	2.20814389	-0.68354164
N	0.71722275	1.63140040	-1.10970179
C	4.33585678	0.52822604	3.37609896
C	0.93186579	4.08253026	-3.60367914
N	-1.11670469	2.02047728	2.11433111
N	-2.30259040	2.57862670	2.37592725
C	-3.24924149	2.19183301	1.48589330
C	-2.59531136	1.33851452	0.62816378
N	-1.29105504	1.26601121	1.06242001
N	-2.19144732	-0.90181040	-2.05025703
N	-3.48466322	-0.63193605	-2.25327909
C	-3.96472766	0.24990790	-1.34234878
C	-2.89229125	0.53116018	-0.52861179
N	-1.82981019	-0.20006502	-1.00962671
C	-2.43479636	3.52294566	3.48579288
C	-4.18316879	-1.22570463	-3.39370972
N	1.75073163	-1.46314098	-2.14618058
N	2.13452178	-2.72296050	-2.37387418
C	1.66928963	-3.57124804	-1.42419326
C	0.95160450	-2.77367592	-0.56379610
N	1.03101024	-1.49077309	-1.05651456
N	-1.08536821	-1.96187175	2.18353327
N	-0.97900909	-3.26994628	2.43666285
C	-0.21266652	-3.90141544	1.51369865

C	0.16836963	-2.91125669	0.63859965
N	-0.39256129	-1.74127399	1.09840350
C	2.99906437	-3.02668671	-3.51463620
C	-1.60423702	-3.83422913	3.63320536
Os	-0.00065172	0.00078198	-0.00251381
H	4.35983195	2.50264576	1.31903579
H	2.98824678	3.92798283	-1.63446119
H	4.70706198	1.46045055	3.79831593
H	5.17050062	-0.07945635	3.02534459
H	3.77336663	-0.01672069	4.12975098
H	1.88353129	4.30686203	-4.08233979
H	0.45782912	5.00533323	-3.26802810
H	0.28136701	3.56735707	-4.30567518
H	-4.26797303	2.53924182	1.53585628
H	-4.98705836	0.59023252	-1.34827631
H	-2.36503437	4.54709348	3.11812990
H	-1.62878311	3.32703398	4.18811289
H	-3.39435512	3.36908169	3.97648242
H	-5.19393794	-1.49885919	-3.09519943
H	-3.63556697	-2.11523292	-3.69391859
H	-4.21760590	-0.51730937	-4.22176163
H	1.87656607	-4.62850630	-1.43986551
H	-0.01022619	-4.95895298	1.55425620
H	2.69659960	-3.97655215	-3.95221580
H	4.03982534	-3.07959855	-3.19379344
H	2.87801297	-2.23163927	-4.24575677
H	-2.01725148	-4.81337889	3.39650411
H	-2.40213682	-3.16337755	3.94075347
H	-0.86890674	-3.92331111	4.43323060

Table S2. Summary of TDDFT vertical excitation data for complexes **1** to **4**.

Complex	Transition	Wavelength / nm (Energy / eV, <i>f</i>)	Composition	Character
1	S ₁	543 (2.28, 0.0023)	HOMO→LUMO	¹ MLCT
	S ₄	482 (2.57, 0.022)	HOMO-1→LUMO	¹ MLCT
	S ₆	443 (2.80, 0.11)	HOMO-1→LUMO+1, HOMO-1→LUMO+2, HOMO-2→LUMO+1 & HOMO-2→LUMO+2	¹ MLCT
	S ₂₂	329 (3.77, 0.10)	HOMO-1→LUMO+7, HOMO-1→LUMO+5 & HOMO-2→LUMO+4	¹ MLCT
	S ₃₈	272 (4.56, 0.46)	HOMO-4→LUMO+1 & HOMO-3→LUMO+2	¹ LC
2	S ₁	518 (2.39, 0.0022)	HOMO→LUMO	¹ MLCT(bpy)
	S ₅	438 (2.83, 0.13)	HOMO-2→LUMO & HOMO-1→LUMO+1	¹ MLCT(bpy)
	S ₆	417 (2.97, 0.047)	HOMO-2→LUMO+1	¹ MLCT(bpy)
	S ₁₈	328 (3.78, 0.090)	HOMO→LUMO+7 & HOMO-1→LUMO+3	¹ MLCT(bpy&btz)
	S ₂₃	314 (3.95, 0.092)	HOMO-2→LUMO+6 & HOMO-2→LUMO+8	¹ MLCT(bpy&btz)
	S ₃₅	272 (4.55, 0.54)	HOMO-4→LUMO	¹ LC(bpy)
3	S ₁	493 (2.51, 0.0014)	HOMO→LUMO	¹ MLCT(bpy)
	S ₃	419 (2.96, 0.10)	HOMO-2→LUMO	¹ MLCT(bpy)
	S ₁₇	318 (3.90, 0.99)	HOMO-1→LUMO+3 & HOMO→LUMO+6	¹ MLCT(bpy&btz)
	S ₂₆	299 (4.14, 0.14)	HOMO-2→LUMO+7 & HOMO-1→LUMO+8	¹ MLCT(btz)
	S ₃₂	273 (4.55, 0.32)	HOMO-3→LUMO & HOMO-5→LUMO	¹ LC(bpy)
4	S ₁	374 (3.31, 0.011)	HOMO→LUMO	¹ MLCT
	S ₅	344 (3.60, 0.018)	HOMO-1→LUMO	¹ MLCT
	S ₁₃	312 (3.98, 0.084)	HOMO→LUMO+8, HOMO-1→LUMO+6 & HOMO-1→LUMO+3	¹ MLCT
	S ₂₂	300 (4.13, 0.13)	HOMO-1→LUMO+6	¹ MLCT
	S ₂₅	295 (4.20, 0.091)	HOMO-1→LUMO+8, HOMO-2→LUMO+7 & HOMO→LUMO+6	¹ MLCT

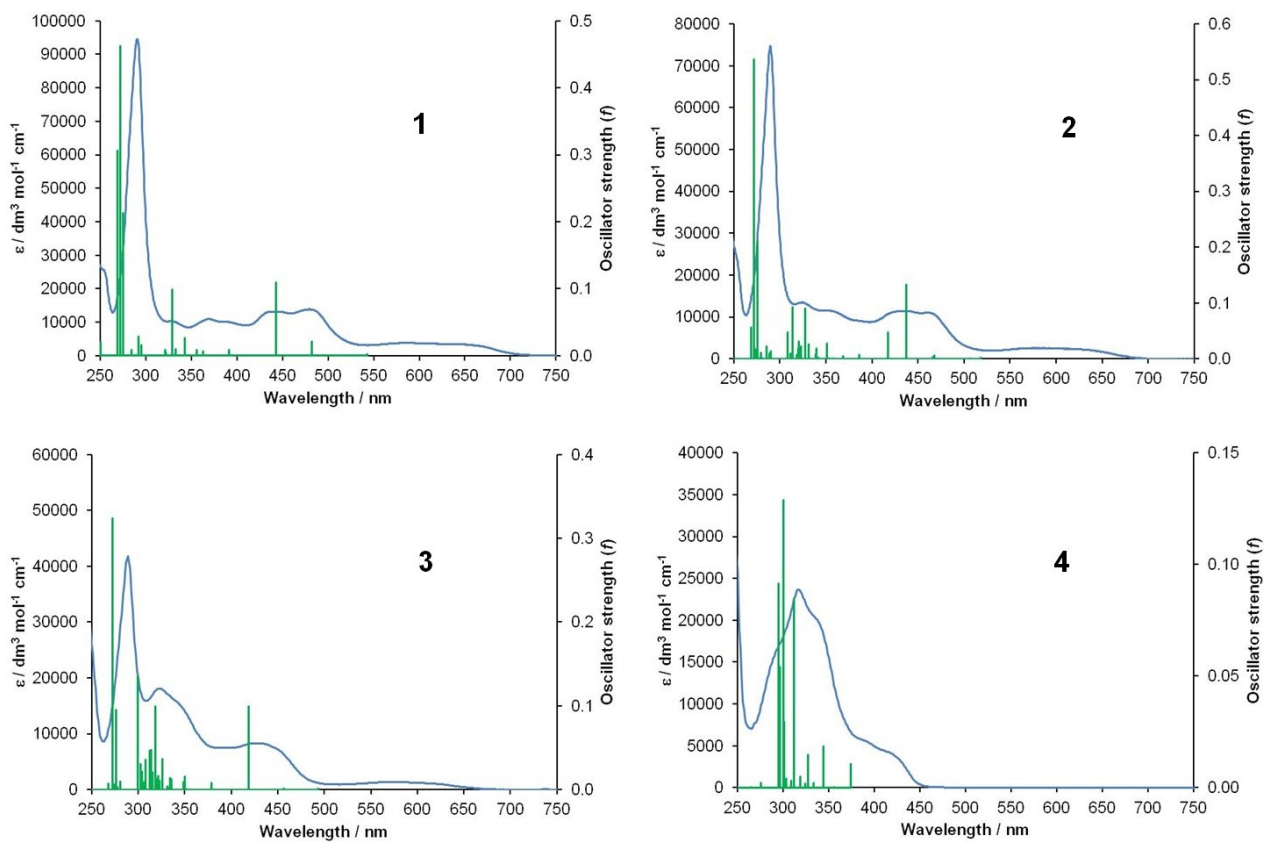


Figure S16: Calculated TDDFT optical absorption spectra for complexes **1** to **4** overlaid with experimental UV-Visible absorption data in acetonitrile solutions.