molecules

MDPI

Supporting Informations

Multistep photochemical reaction of polypyridine-based ruthenium nitrosyl complexes in dimethylsulfoxide

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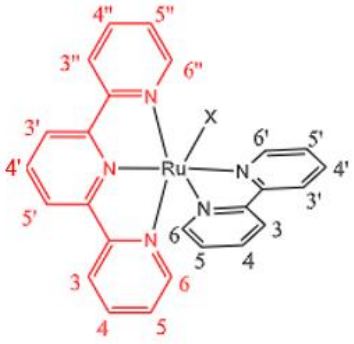
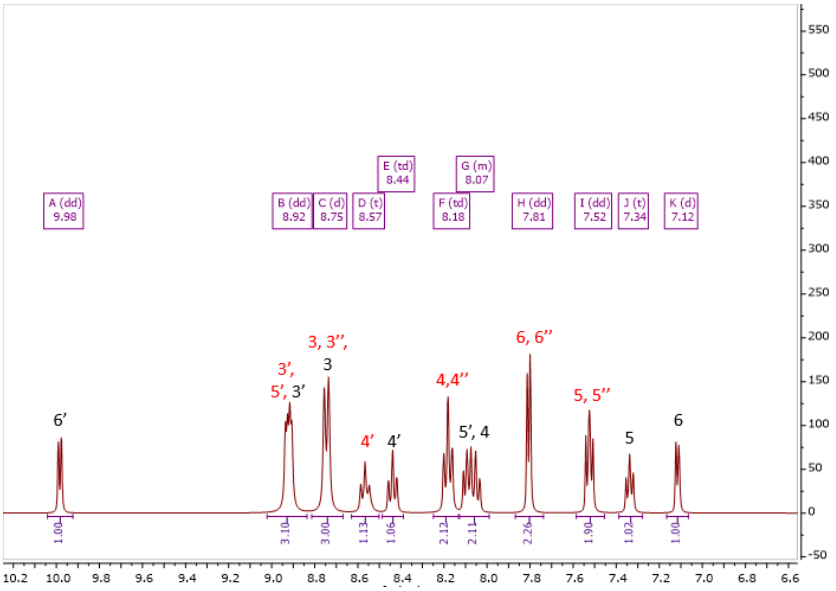
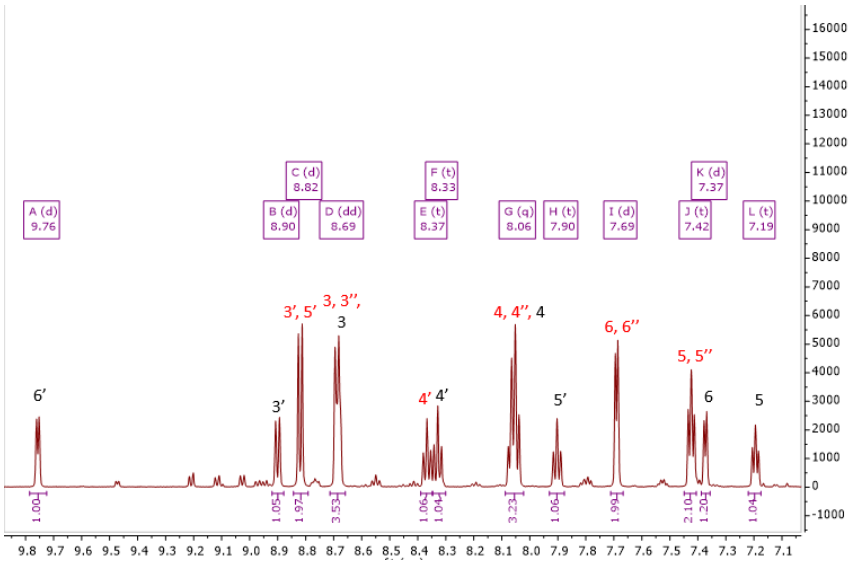


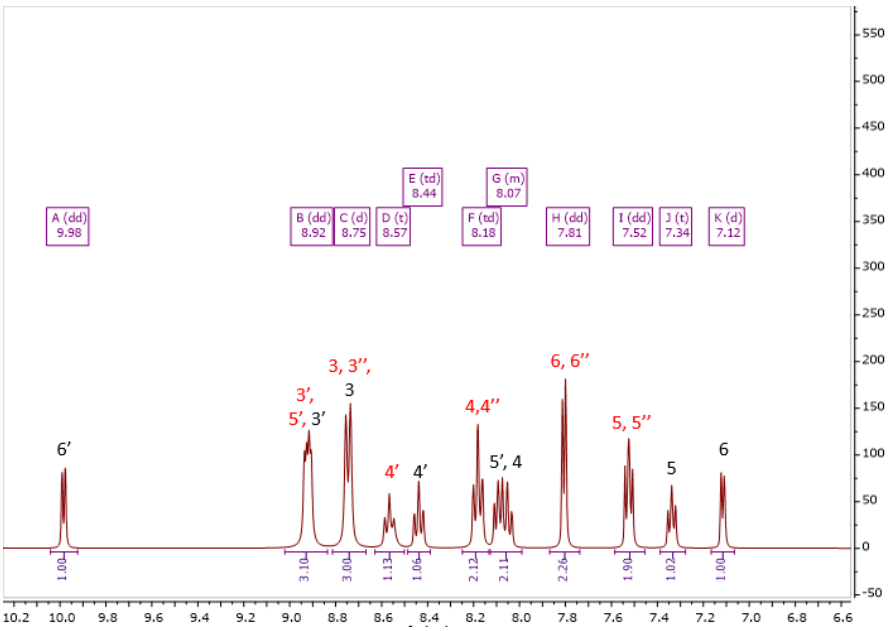
Figure 1. Assignment of ^{1}H-NMR signals for [RuT0B0(NO)](PF$_6$)$_3$ (in DMSO).



Form A.



Form B.


A (dd) 9.98
B (dd) 8.92
C (d) 8.75
D (t) 8.57
E (td) 8.44
F (td) 8.18
G (m) 8.07
H (dd) 7.81
I (dd) 7.52
J (t) 7.34
K (d) 7.12
6'
3', 5', 3'
3, 3'', 3
4'
4' 4'
4,4''
5', 4
6, 6''
5, 5''
5
6
1.00
3.10
3.00
1.13
1.06
2.12
2.11
2.26
1.90
1.02
1.00

Form C.

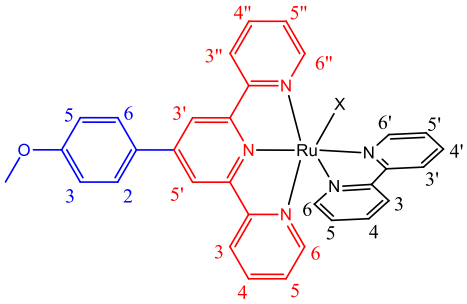
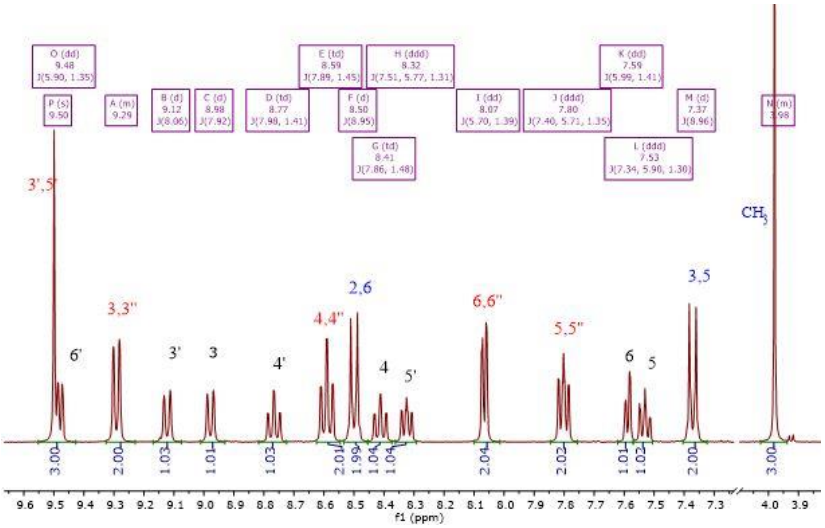
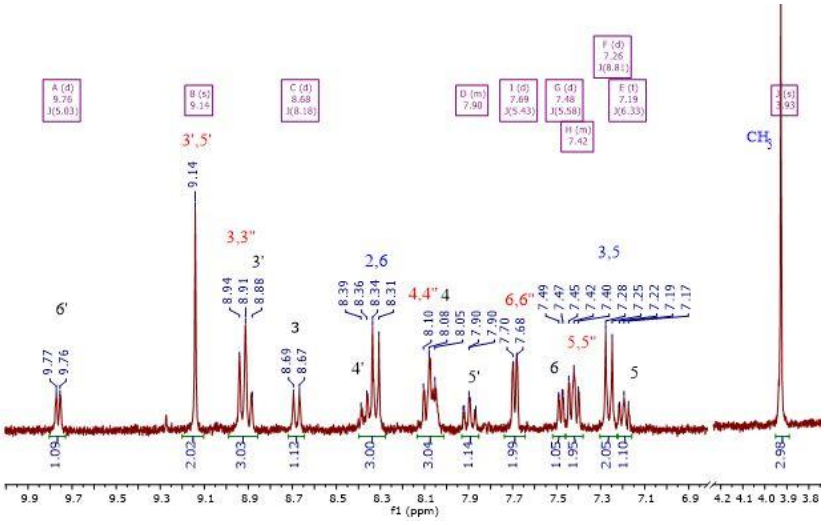


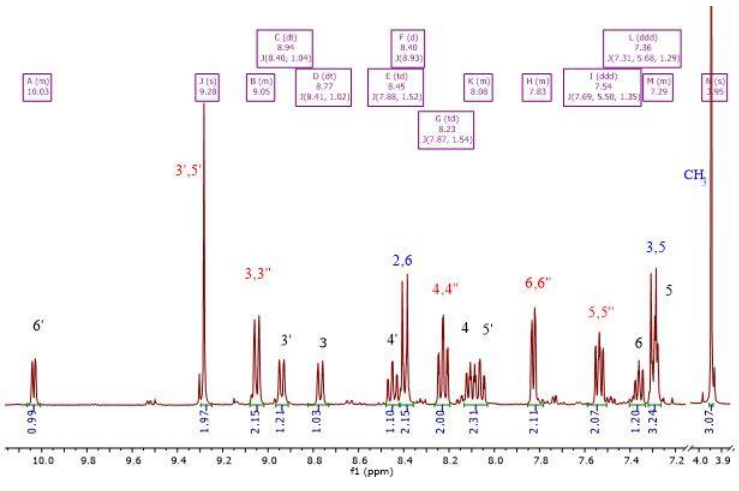
Figure 2. Assignment of ^{1}H-NMR signals for [RuT1B0(NO)](PF$_6$)$_3$ (in DMSO).



Form A.

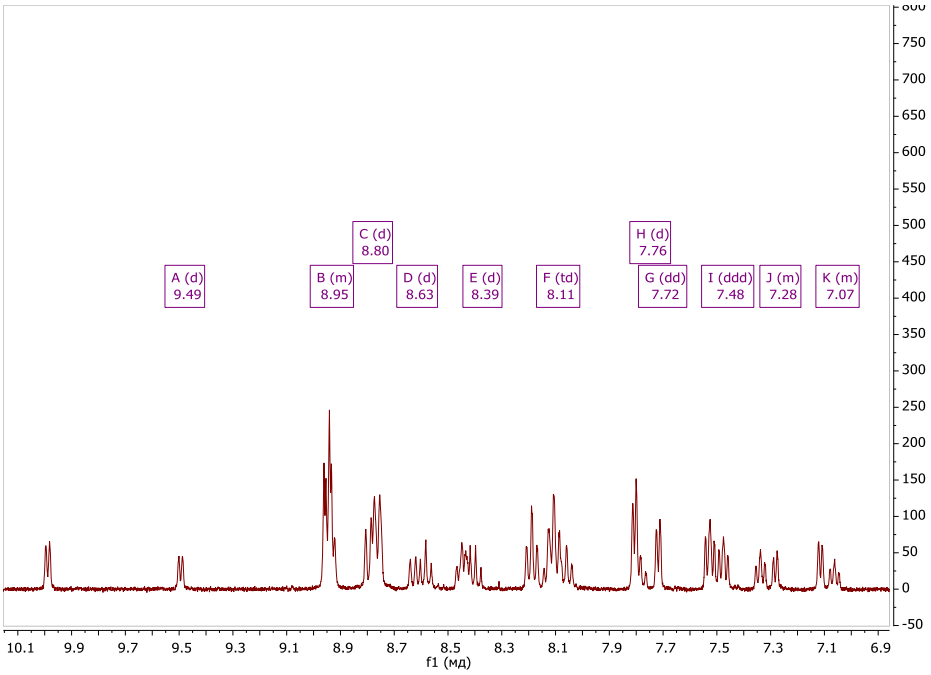


Form B.

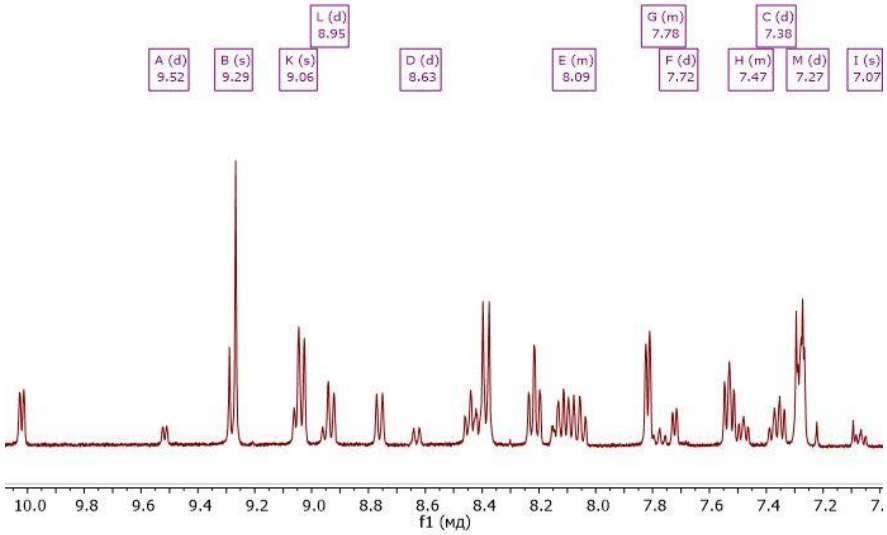

A (m) 10.03
J (s) 9.28
B (m) 9.05
C (dt) 8.96 J(8.40, 1.04)
D (dt) 8.77 J(8.41, 1.02)
E (td) 8.45 J(7.88, 1.52)
F (d) 8.40 J(8.93)
G (td) 8.23 J(7.87, 1.54)
K (m) 8.08
H (m) 7.83
I (ddd) 7.54 J(7.69, 5.50, 1.35)
L (ddd) 7.36 J(7.31, 5.68, 1.29)
M (m) 7.29
N (s) 3.95
3',5'
3,3''
2,6
4,4''
6,6''
5,5''
3,5
CH3
6'
3'
3
4'
4
5'
5
6
0.99
1.97
2.15
1.21
1.03
1.10
2.15
2.00
2.31
2.11
2.07
1.20
3.24
3.07
10.0 9.8 9.6 9.4 9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 4.0 3.9
f1 (ppm)

Form C.

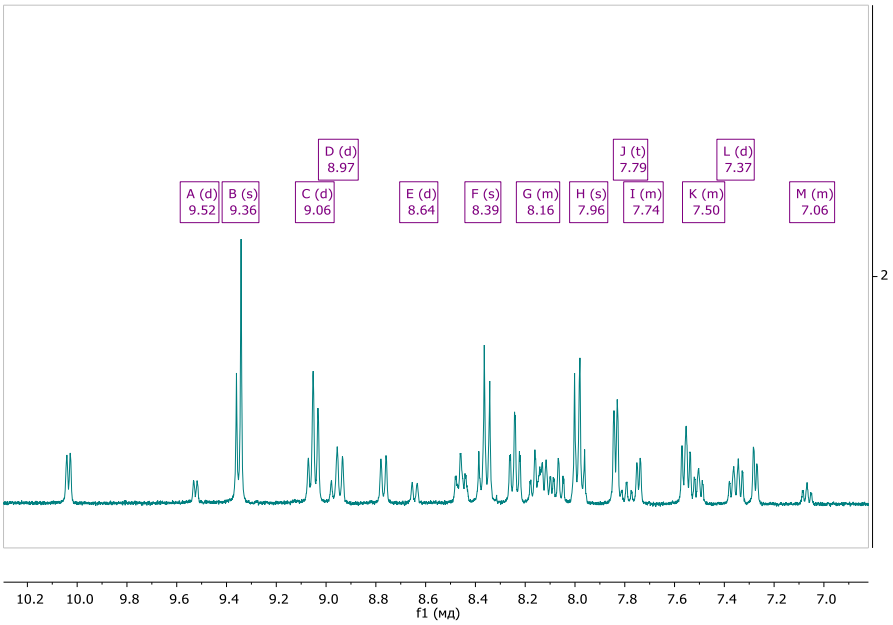
Figure 3. [1]H-NMR ((400 MHz, DMSO-d6) of form D, obtained from a C/D mixture after irradiation of form C in DMSO, at = 365 nm.



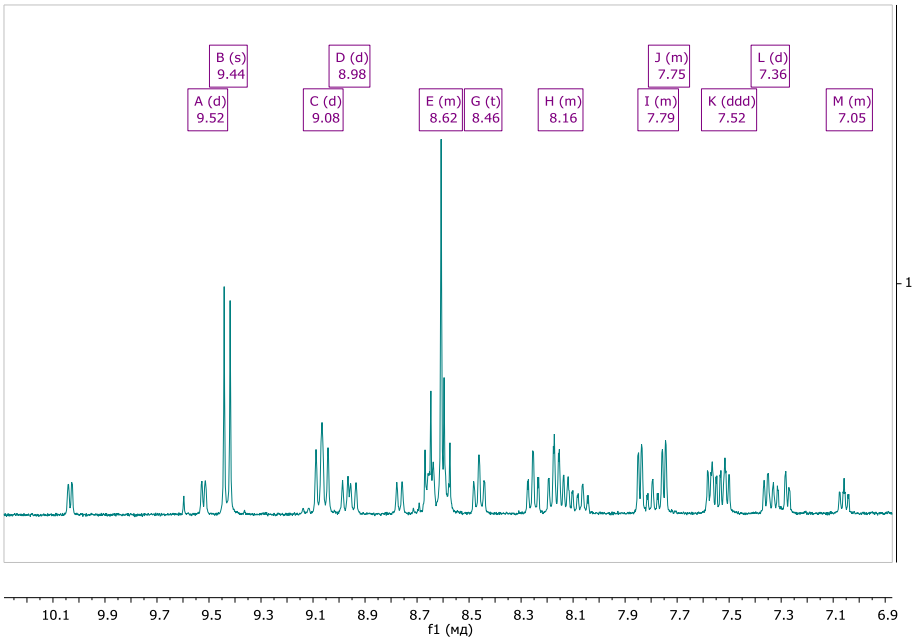
[RuT0B0(DMSO)$_{(S)}$](PF$_6$)$_2$.



[RuT1B0(DMSO)$_{(S)}$](PF$_6$)$_2$.



[RuT2B0(DMSO)$_{(S)}$](PF$_6$)$_2$.



[RuT3B0(DMSO)$_{(S)}$](PF$_6$)$_2$.

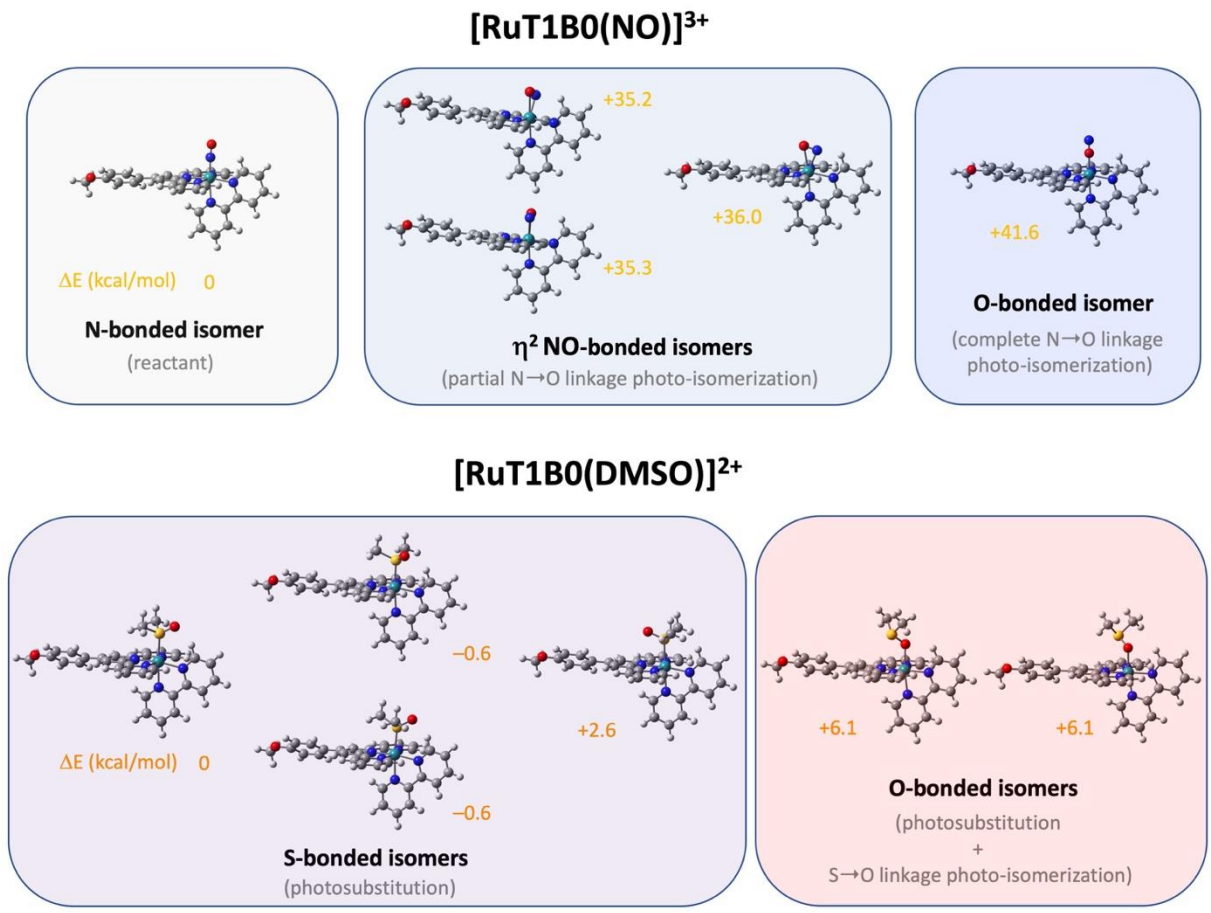


Figure 4. Computed structures of $[RuT1B0(NO)]^{3+}$ and $[RuT1B0(DMSO)]^{2+}$ complexes at the DFT level of theory and relative energies (in kcal/mol) of the different isomers.

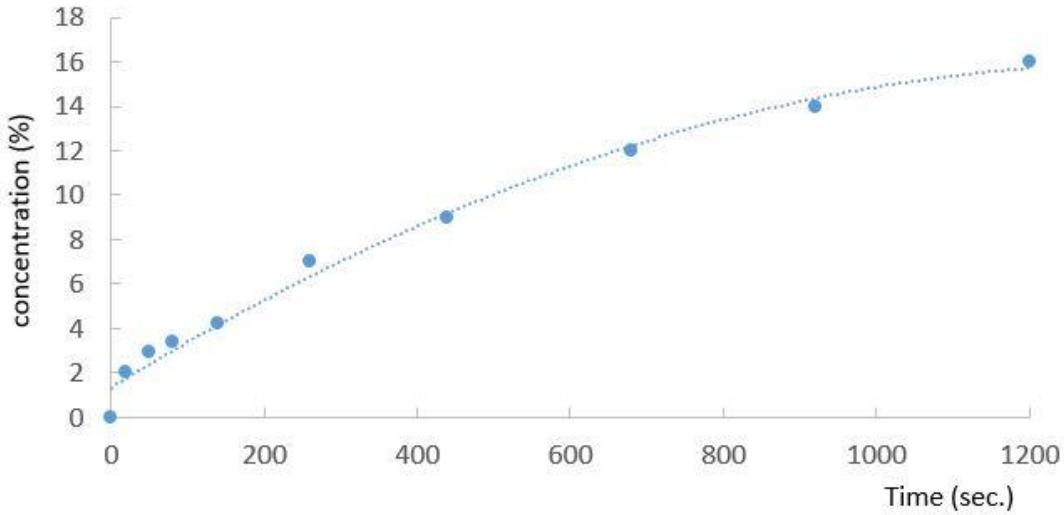
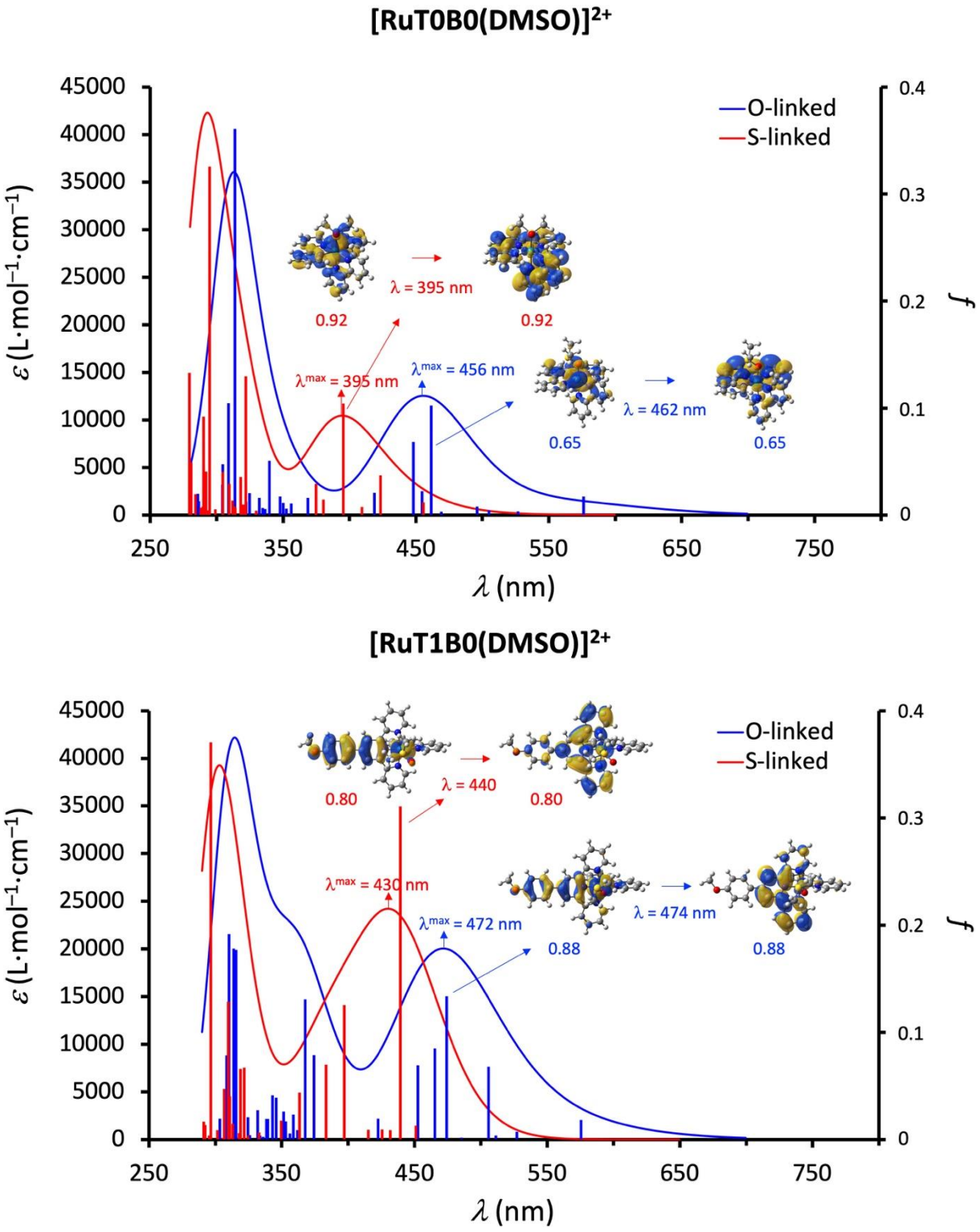
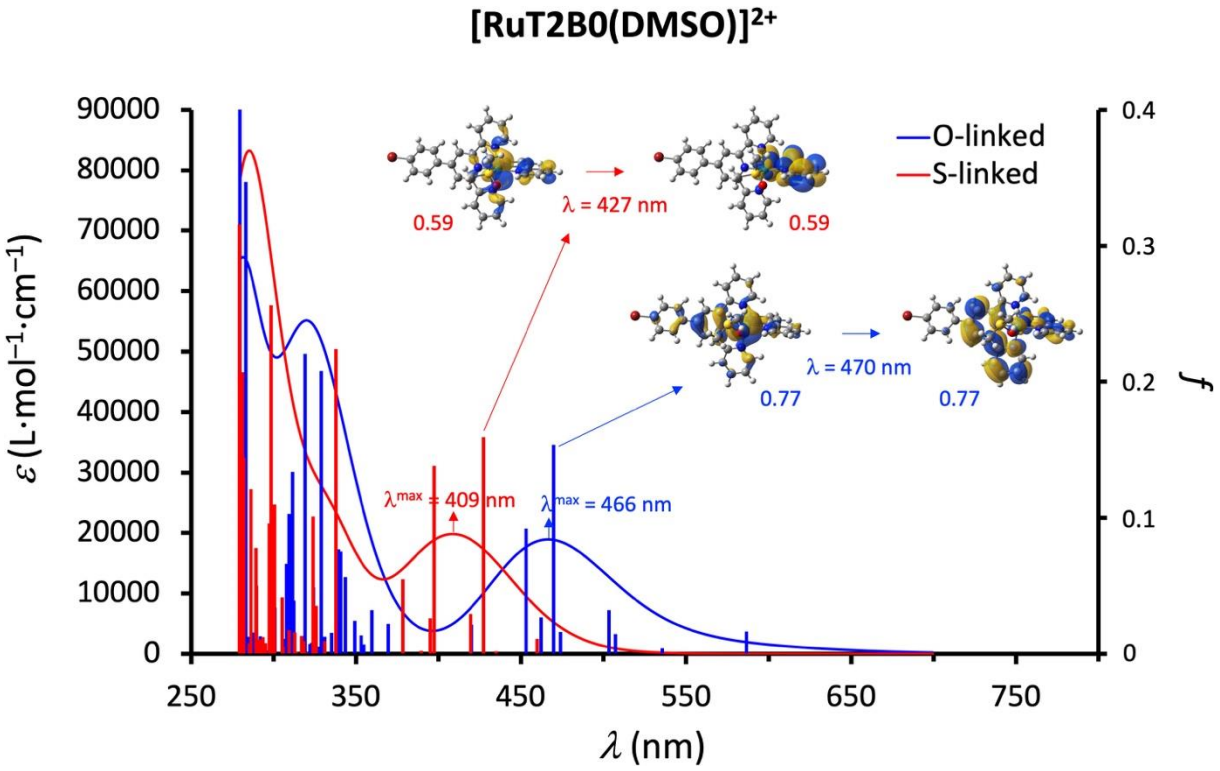
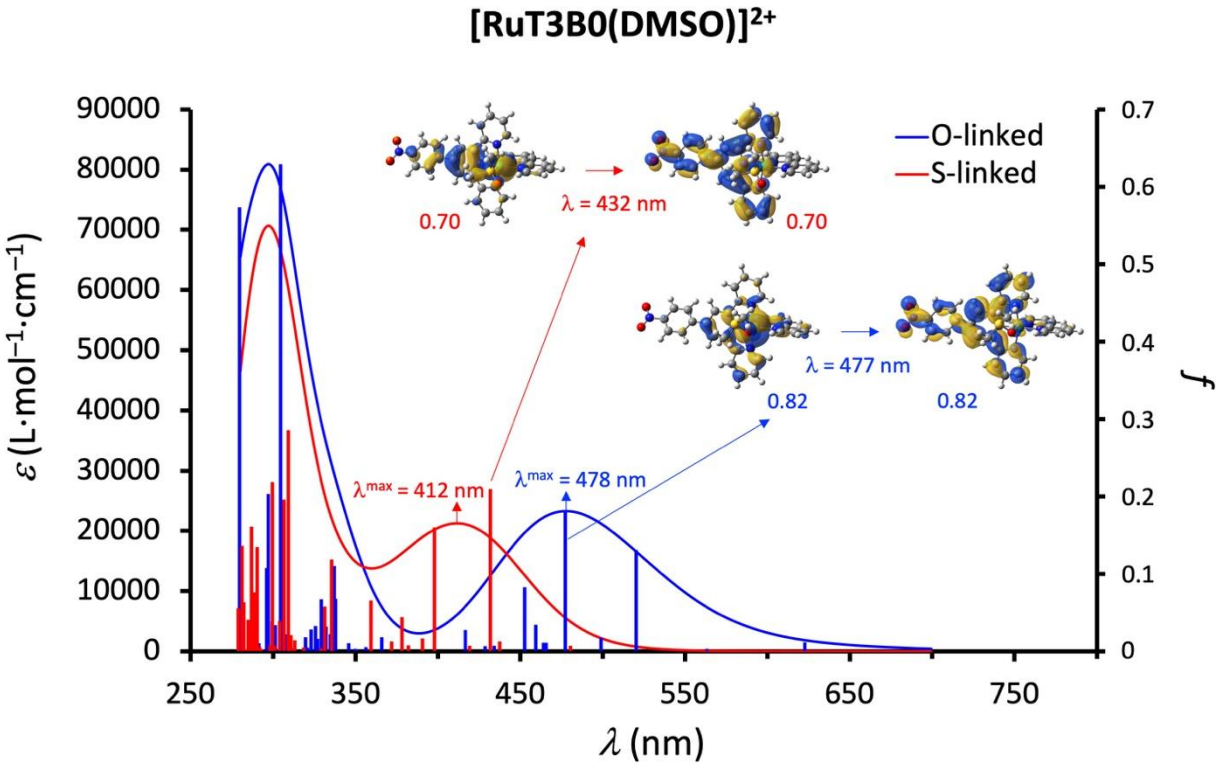


Figure 5. Relative concentration of [RuT1B0(DMSO$_{(5)}$)](PF$_6$)$_2$ (form C) from irradiation of [RuT1B0(NO)](PF$_6$)$_3$ (form A) in DMSO, estimated from ^{1}H-NMR tracking.

Figure 6. Simulated absorption spectra of S- and O-bonded $[RuT0B0(DMSO)]^{2+}$, $[RuT1B0(DMSO)]^{2+}$, $[RuT2B0(DMSO)]^{2+}$and $[RuT3B0(DMSO)]^{2+}$ complexes at the TD-DFT level of theory. Analysis of the lowest energy absorption band is given in terms of natural transition orbitals.




[RuT2B0(DMSO)]2+
O-linked
S-linked
λ = 427 nm
0.59
0.59
λ = 470 nm
0.77
0.77
λmax = 409 nm
λmax = 466 nm
ε (L·mol−1·cm−1)
f
λ (nm)


[RuT3B0(DMSO)]2+
O-linked
S-linked
λ = 432 nm
0.70
0.70
λ = 477 nm
0.82
0.82
λmax = 412 nm
λmax = 478 nm
ε (L·mol−1·cm−1)
f
λ (nm)