Electronic Supplementary Material (ESI) for Dalton Transactions.

:Two Ruthenium Complexes Capable of Storing Multiple Electrons on a Single Ligand - Photophysical, Photochemical and Electrochemical properties of $[Ru(phen)_2(TAPHAT)]^{2+}$ and $[Ru(phen)_2(TAPHAT)Ru(phen)_2]^{4+}$.

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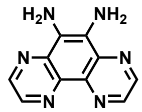
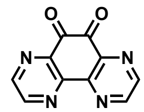
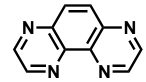
Structures of ligands



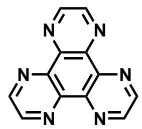
1,4,5,8-tetraazaphenanthrene-9,10-diamine
"diNH$_2$TAP"



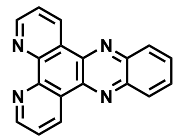
1,4,5,8-tetraazaphenanthrene-9,10-dione
"TAPdione"



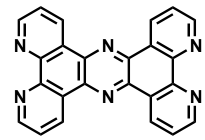
1,4,5,8-tetraazaphenanthrene
"TAP"



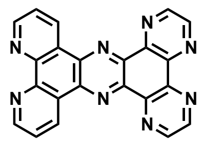
1,4,5,8,9,12-hexaazatriphenylene
"HAT"



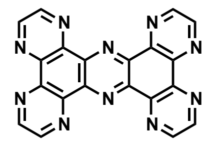
dipyrido[3,2-a:2',3'-c]phenazine
"DPPZ"



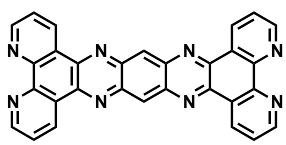
Tetrapyrido[3,2-a:2',3'-c:3'',2''-h:2''',3'''-j]phenazine
"TPPHZ"



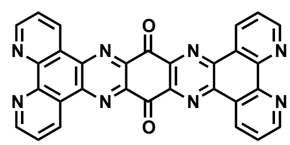
1,10-phenanthrolino[5,6-b]1,4,5,8,9,12-hexaazatriphenylene
"PHEHAT"



1,4,5,8-tetraazaphenanthrene[9,10-b]1,4,5,8,9,12-hexaazatriphenylene
"TAPHAT"



9,11,20,22-tetraazatetrapyrido[3,2-a:2',3'-c:3'',2''-l:2''',3'''-n]-pentacene
"TATPP"



9,11,20,22-tetraazatetrapyrido[3,2-a:2',3'-c:3'',2''-l:2''',3'''-n]-pentacene-10,21-quinone
"TATPP"

Figure S1: Structures of the different ligands reported in this study.

Mass spectrometry

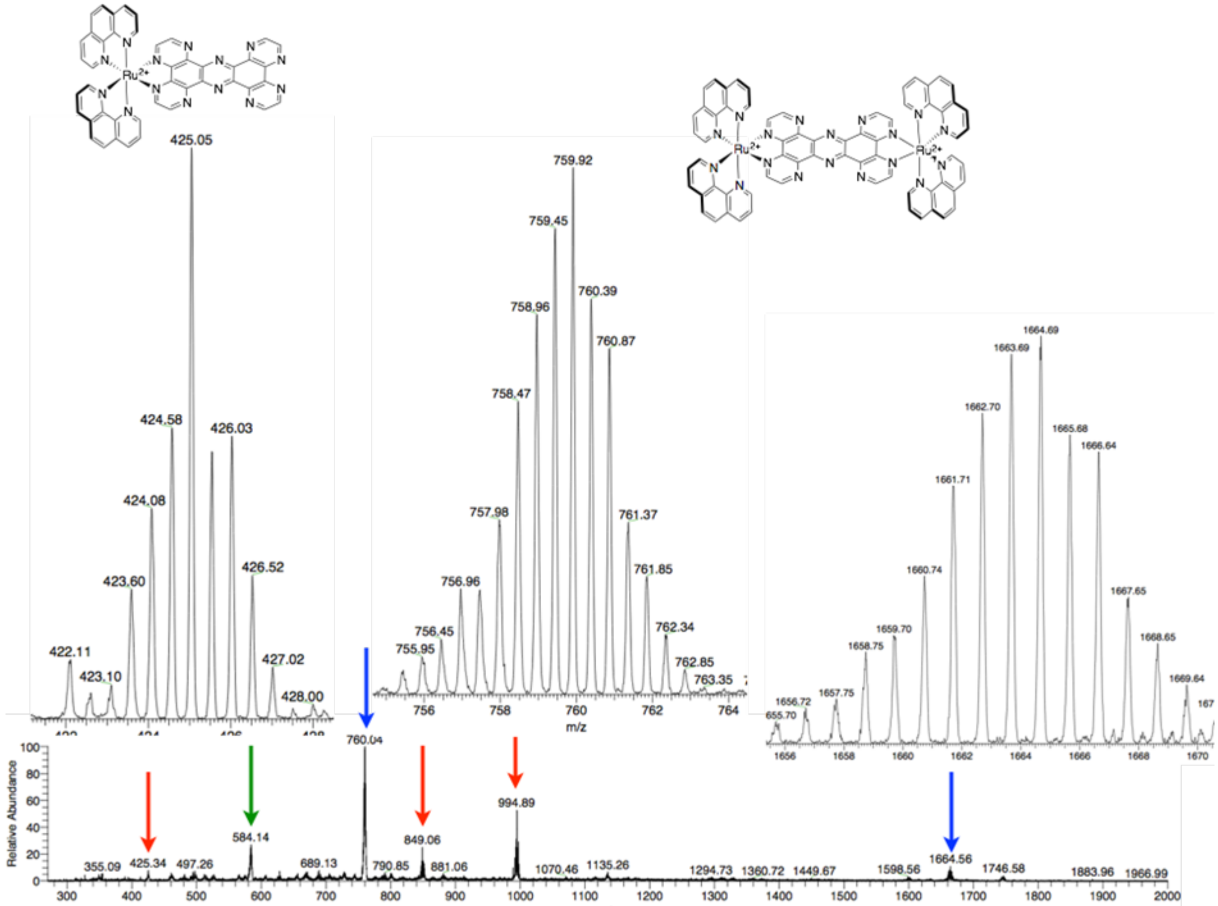


Figure S2: ESI-MS spectrum that shows the formation of mono and dinuclear complexes upon reaction between [Ru(phen)$_2$Cl$_2$] and TAPHAT. This mixture of products is not obtained when starting from precursor complex [Ru(phen)$_2$(diNH$_2$TAP)]$^{2+}$ (see below).

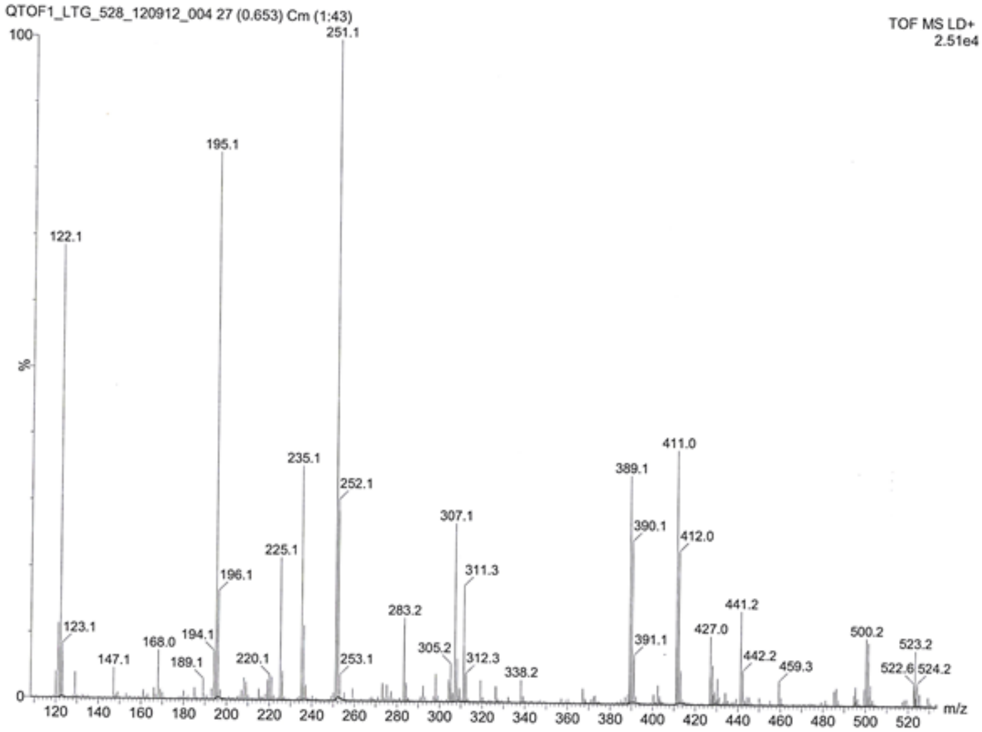


Figure S3: EI-MS spectrum of TAPHAT recorded from THF solutions.

Table S1: Peaks of interest obtained from figure S3. Peaks present at m/z = 122.1, 195.1 and 251.1 have not been taken into consideration as they were already present in the neat solvent used for this study.

m/z measured	Attribution	m/z calculated	Relative Intensity
389.1	$[M+H^+]^+$	389.10	34%
411.0	$[M+Na^+]^+$	411.08	39%
427.0	$[M+K^+]^+$	427.06	10%

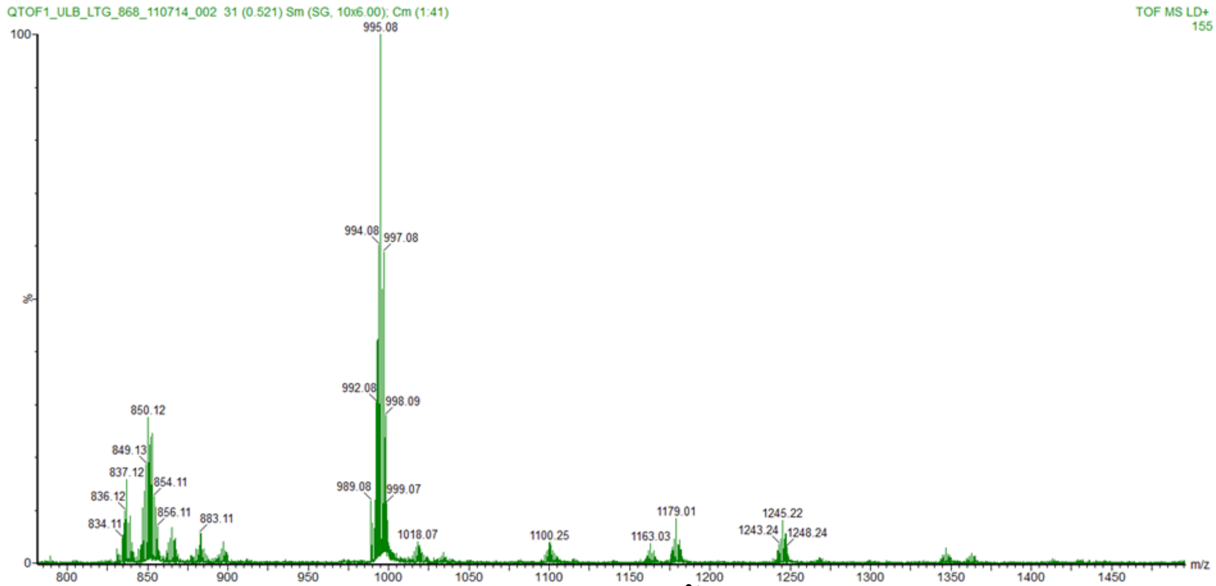


Figure S4: MALDI-MS spectrum of $[Ru(phen)_2(TAPHAT)]^{2+}.2PF_6^-$

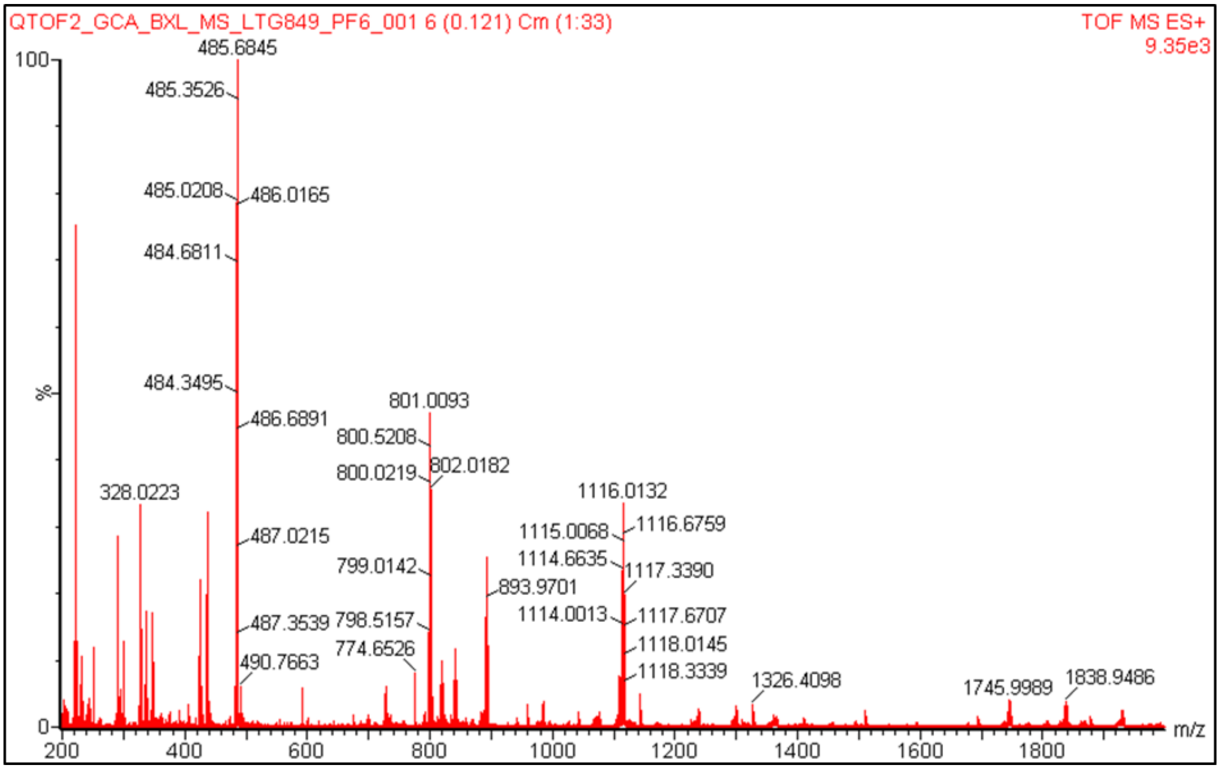


Figure S5: ESI-MS spectrum of $[Ru(phen)_2(TAPHAT)Ru(phen)_2]^{4+}.4PF_6^-$

Table 5: Peaks of interest obtained from figure S10.

m/z measured	Attribution	m/z calculated	Relative Intensity
328.02	$[M^{4+}]^{4+}$	328.04	35 %
425.05	$[M^{4+} - [Ru(phen)_2]^{2+}]^{2+}$	425.07	22 %
437.03	$[M^{4+} - H^+]^{3+}$	437.06	32 %
485.68	$[M^{4+} + PF_6^-]^{3+}$	485.38	100 %
801.01	$[M^{4+} + 2PF_6^-]^{2+}$	801.05	48 %
893.97	$[M^{4+} + 3PF_6^- + K^+]^{2+}$	893.52	26 %
1116.01	$[2M^{4+} + 5PF_6^-]^{3+}$	116.06	34 %
1746.00	$[2M^{4+} + 6PF_6^-]^{2+}$	1746.57	6 %
1838.95	$[2M^{4+} + 7PF_6^- + K^+]^{2+}$	1838.53	6 %
1929.92	$[2M^{4+} + 8PF_6^- + 2K^+]^{2+}$	1930.50	4 %

NMR spectroscopy

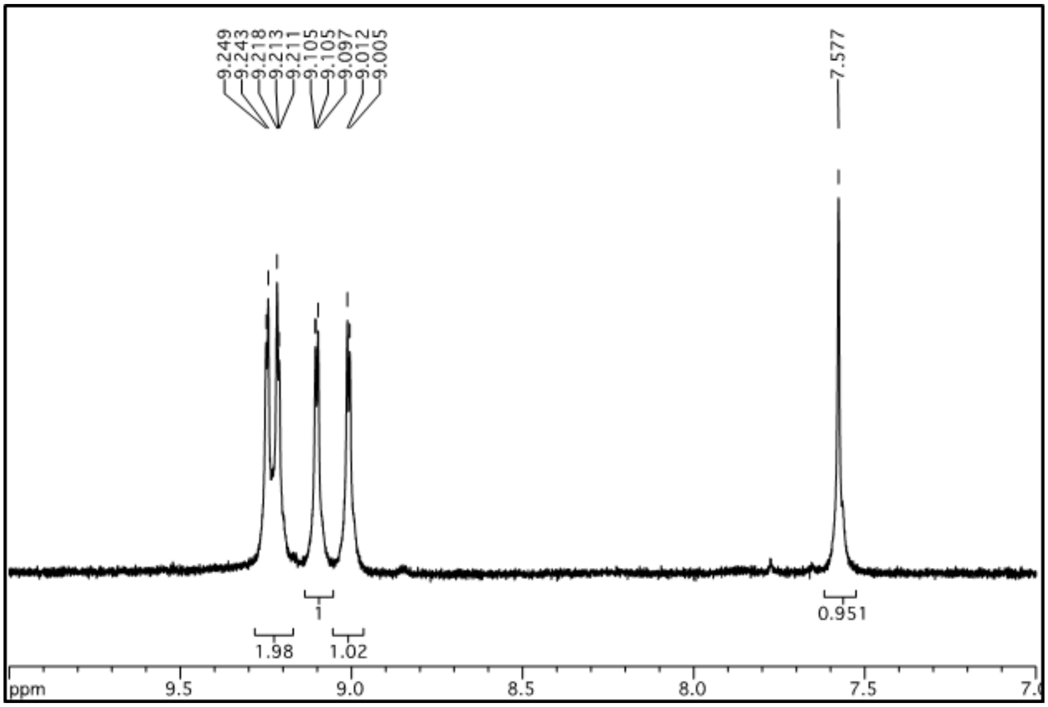


Figure S6: ^{1}H NMR of 9-hydroxy-1,4,5,8-tetraazaphenanthrene recorded in CD_3OD at 300MHz

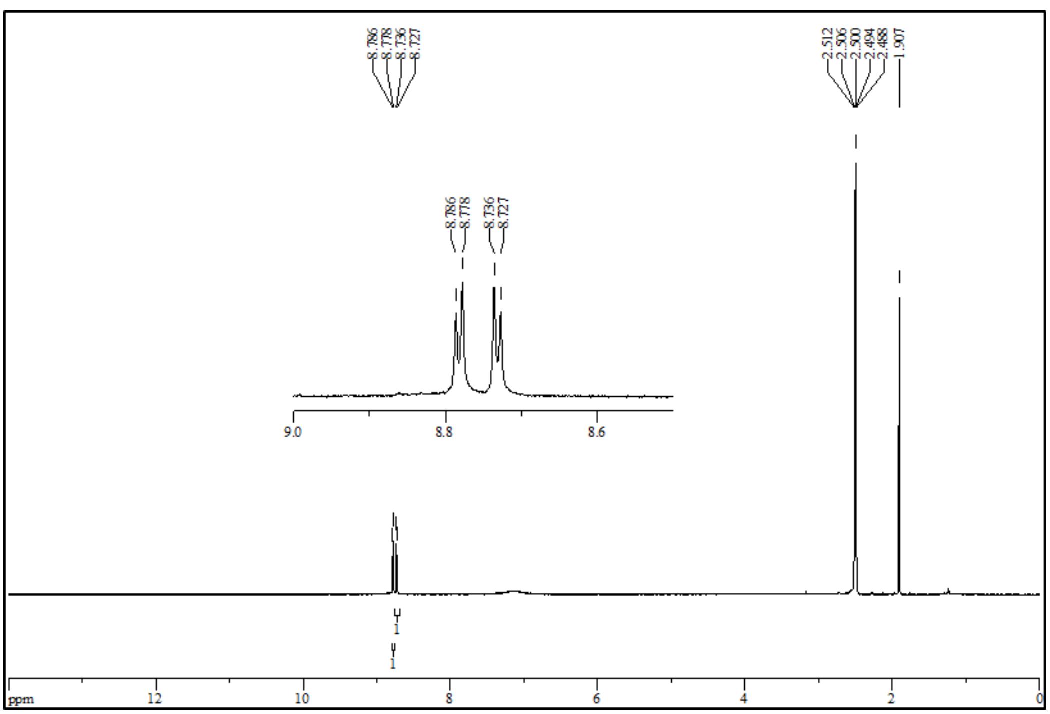


Figure S7: ^{1}H NMR of 1,4,5,8-tetraazaphenanthrene-9,10-dione recorded in DMSO-d_6 at 300MHz

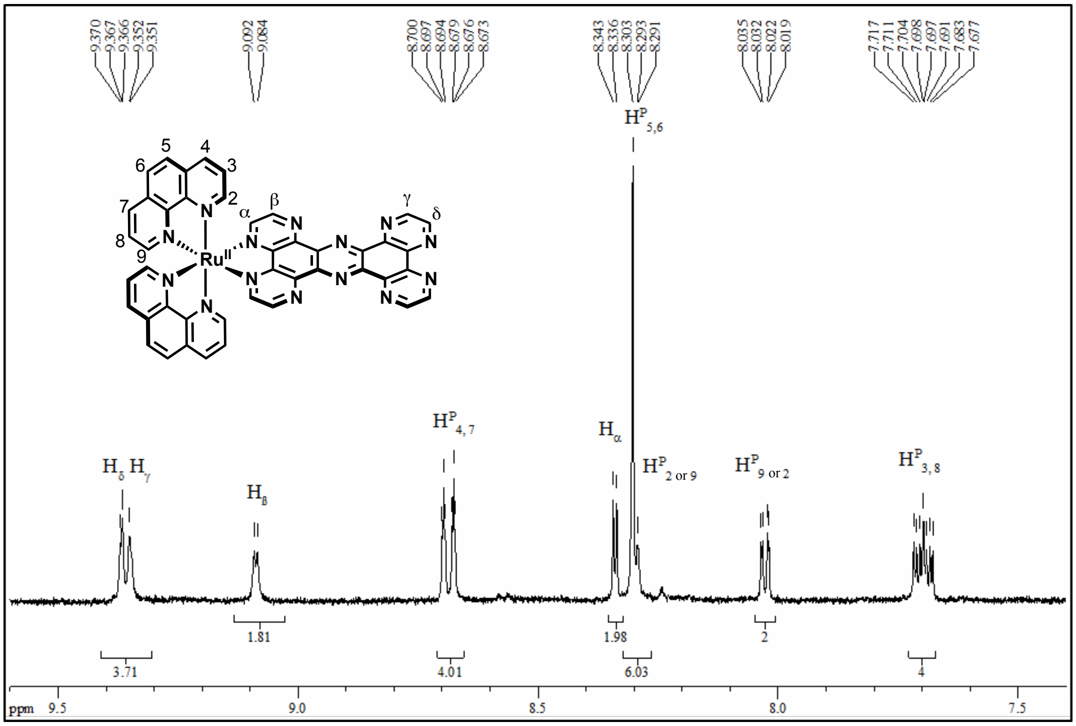


Figure S8: ^{1}H NMR of $[Ru(phen)_2(TAPHAT)]^{2+}.2PF_6^-$ recorded in CD_3CN at 300MHz

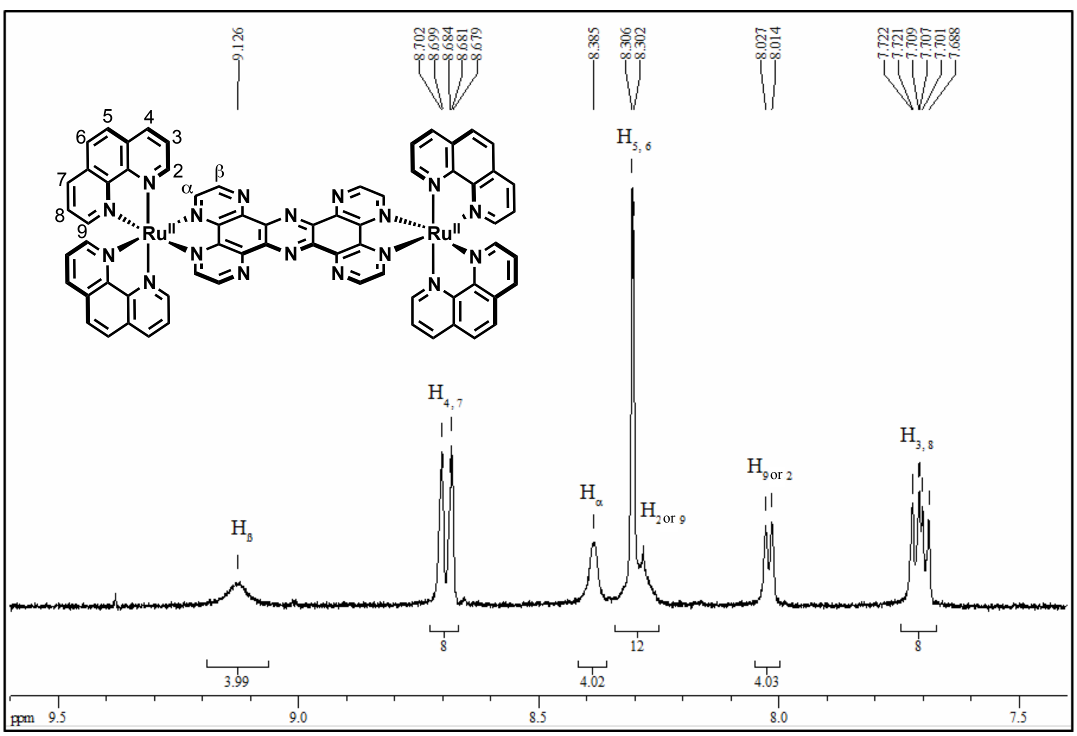


Figure S2: ^{1}H NMR of $[Ru(phen)_2(TAPHAT)Ru(phen)_2]^{4+}.4PF_6^-$ recorded in CD_3CN at 300MHz

Photostability measurement

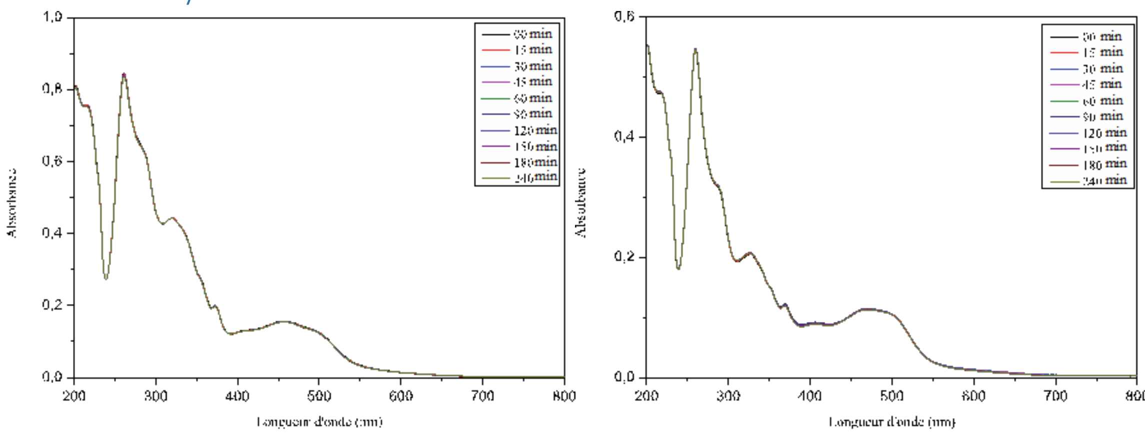


Figure S10: Photostability of [Ru(phen)$_2$(TAPHAT)]$^{2+}$.2PF$_6^-$ (left) and [Ru(phen)$_2$(TAPHAT)Ru(phen)$_2$]$^{4+}$.4PF$_6^-$ (right) under light irradiation (Xe, 200W) in acetonitrile and at room temperature

Infrared spectroscopy

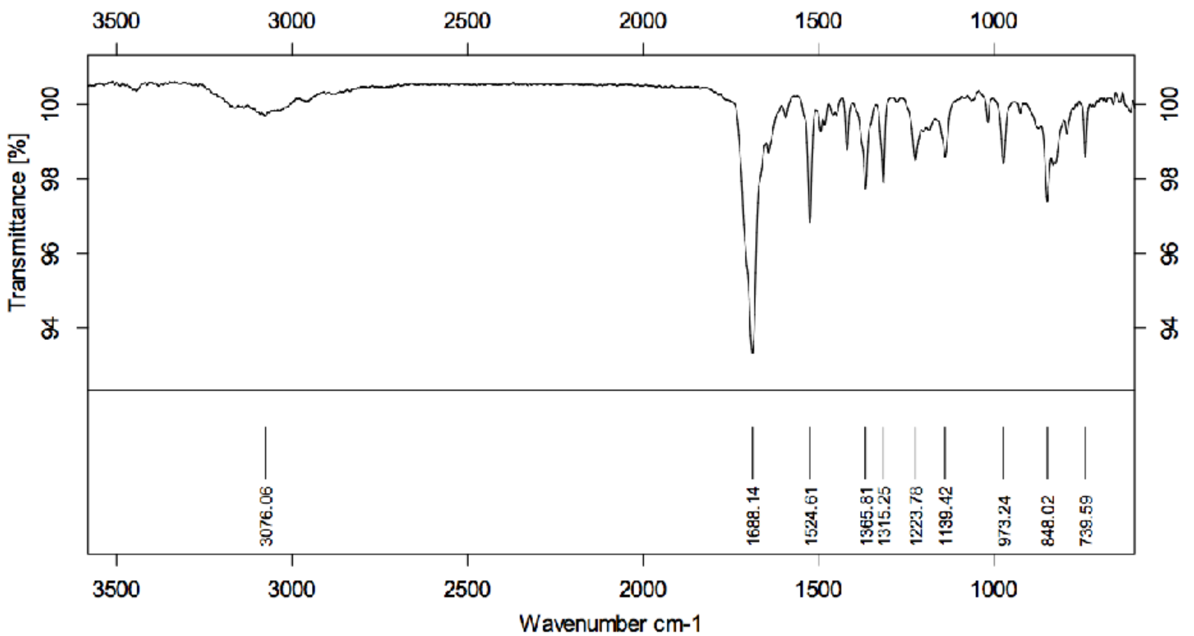


Figure S11: IR spectrum of 1,4,5,8-tetraazaphenanthrene-9,10-dione