Electronic supplementary information

Theoretical exploration of the photophysical properties of two-component RuII-Porphirin dyes as promising assemblies for a combined antitumor effect

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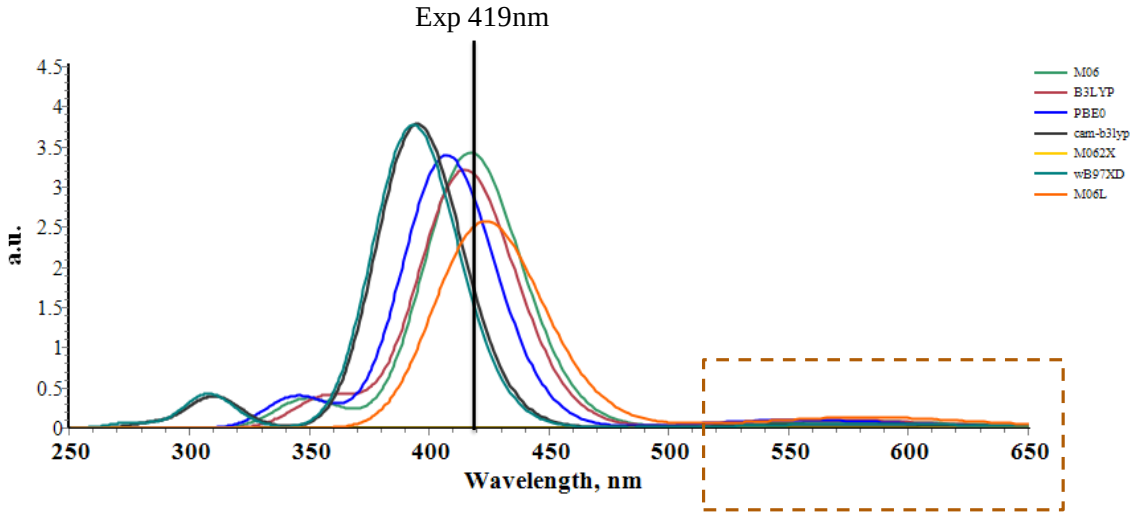
a) UV-Vis spectrum and **b)** main absorption wavelengths calculated for compound **Ru-*m*3a** by using the 6-31G*/SDD basis set and different XC functionals in dichloroMethane (ε=8.93) compared with experimental data available in literature.[1]

a)

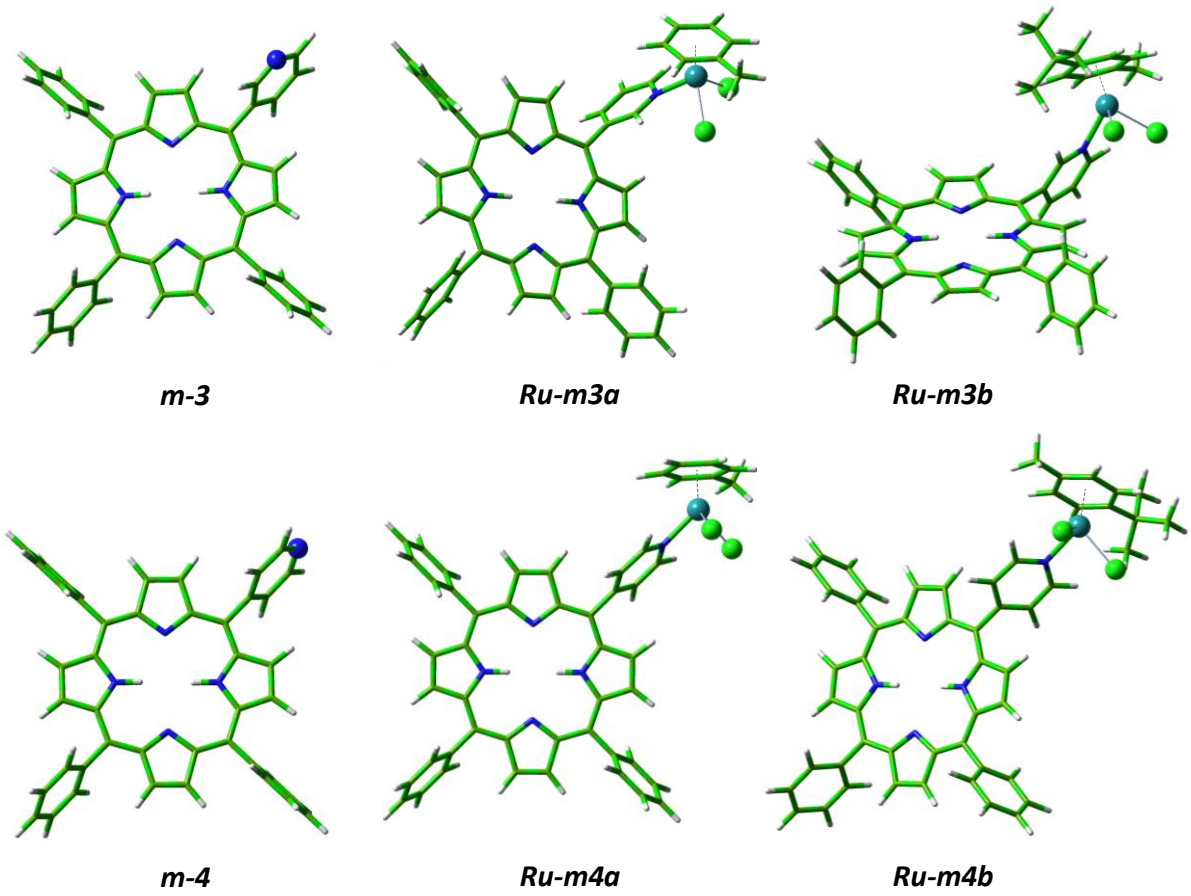


b)

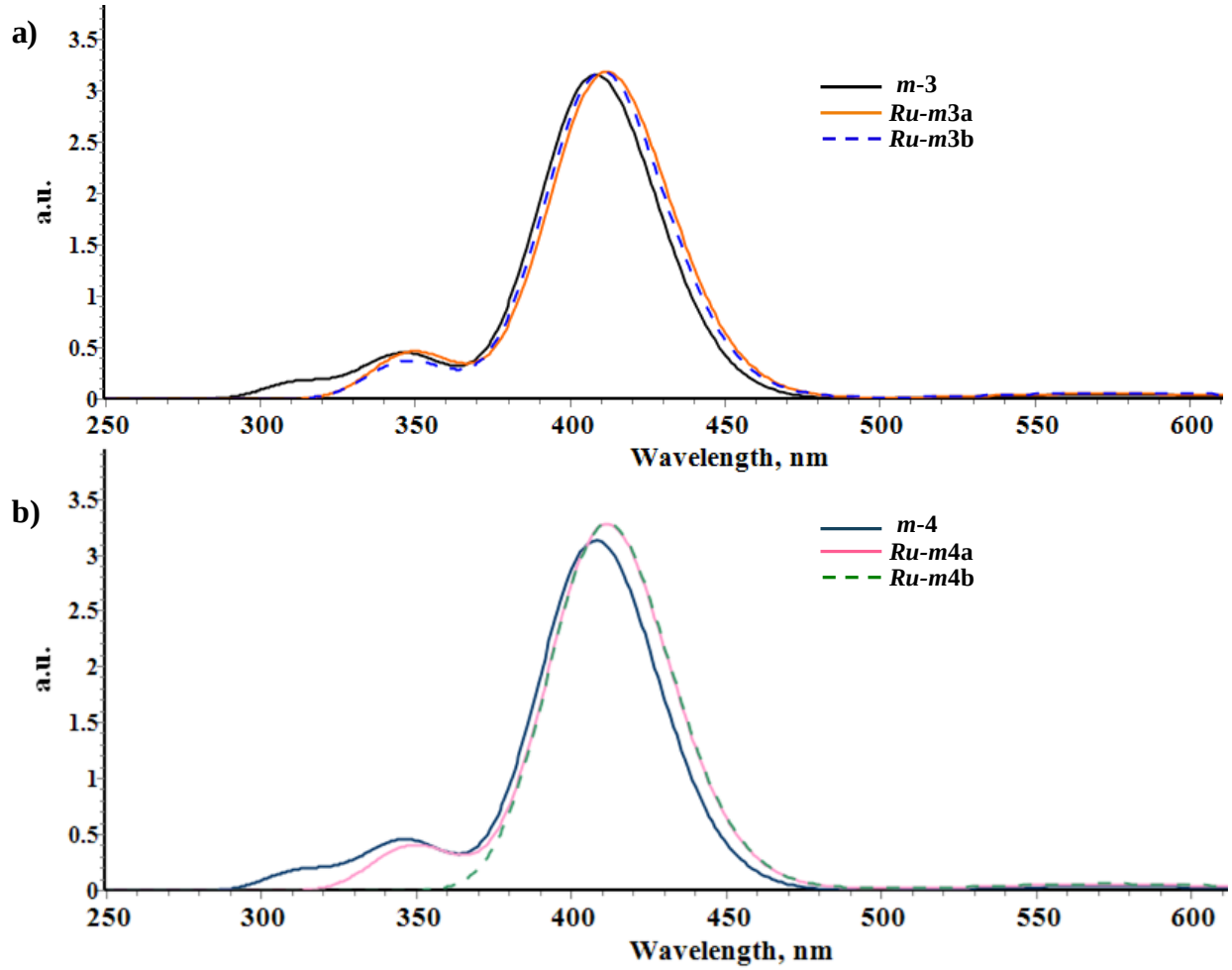
	B band		Q1 band		Q2 band	
XC Functional	***λ nm*** ***(f)***	***Main Configuration***	***λ nm*** ***(f)***	***Main Configuration***	***λ nm*** ***(f)***	***Main Configuration***
B3LYP	**417** *(1.1052)*	H-1→L+1	**549** *(0.0623)*	H-1→L	**584** *(0.0561)*	H→L
Cam-B3LYP	**394** *(1.9246)*	H-1→L+1	**551** *(0.0347)*	H-1→L	**601** *(0.0286)*	H→L
M06	**419** *(1.5111)*	H-1→L+1	**564** *(0.0463)*	H-1→L	**596** *(0.0427)*	H→L
M06L	**427** *(1.2082)*	H-2→L	**569** *(0.0666)*	H-1→L	**606** *(0.0321)*	H-1→L
PBE0	**409** *(1.4337)*	H-1→L+1	**539** *(0.061)*	H-1→L	**574** *(0.00527)*	H→L
M062X	**396** *(1.4579)*	H-1→L+1	**530** *(0.0433)*	H-1→L	**580** *(0.0308)*	H→L
wB97XD	**395** *(1.8494)*	H-1→L+1	**562** *(0.0366)*	H-1→L	**617** *(0.00287)*	H→L
Exp [1]	**419**		**515, 550**		**589, 645**	

1] J Biol Inorg Chem, 2009, 14:101–109

Optimized structures of the compounds ***m*-3, Ru-*m*3a, Ru-*m*3b, *m*-4, Ru-*m*4a, Ru-*m*4b** under investigation, obtained in water at B3LYP/6-31+G(d,p)/SDD//6-311++G(2df,2p) level of theory;



UV-Vis Spectra of **a) *m*-3, Ru-*m*3a, Ru-*m*3b** and **b) *m*-4, Ru-*m*4a, Ru-*m*4b,** calculated in water at M06/6-31+G(d,p)/SDD level of theory; Available experimental data in literature are reported below.

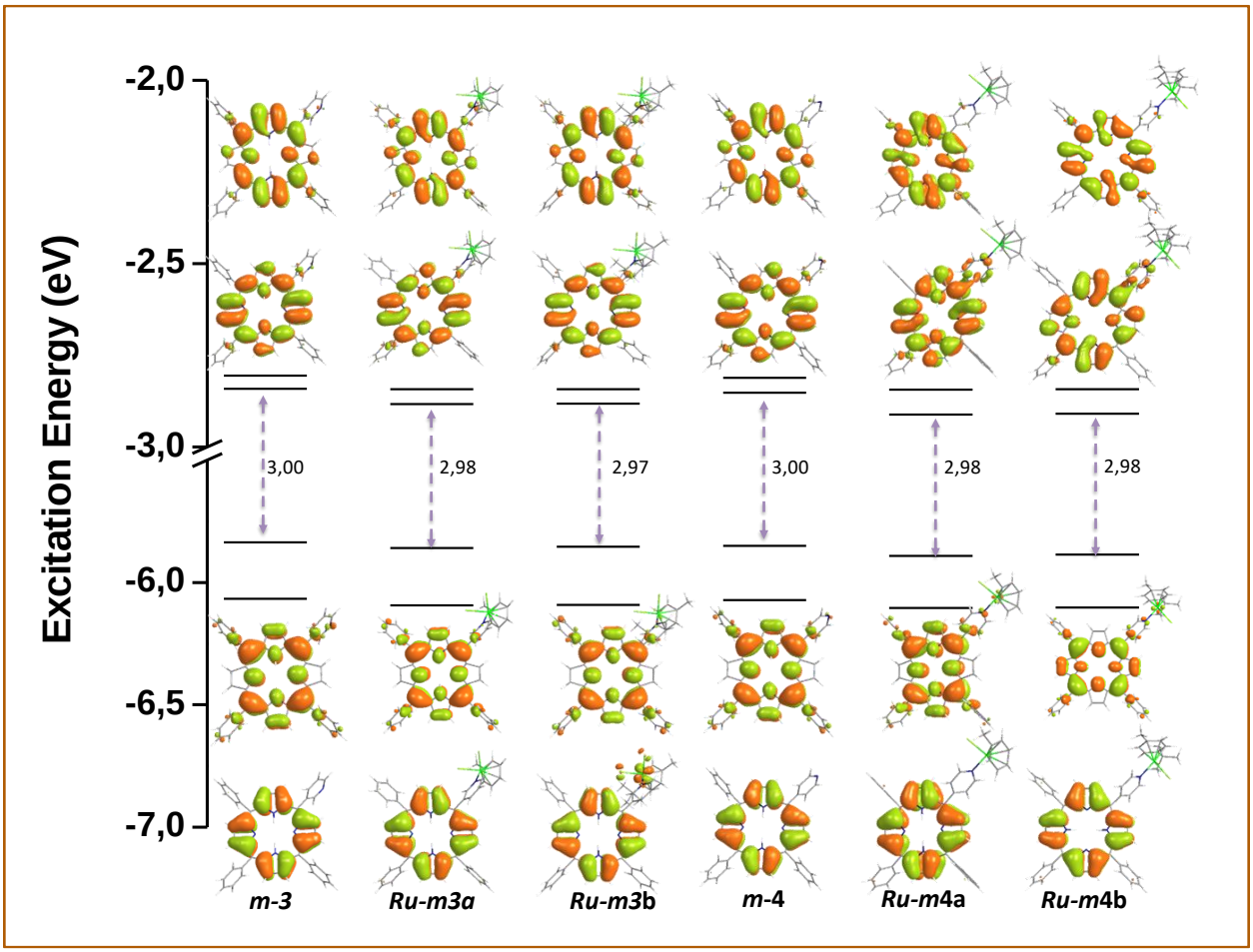


Experimental Data in CH_2Cl_2 [1,2]

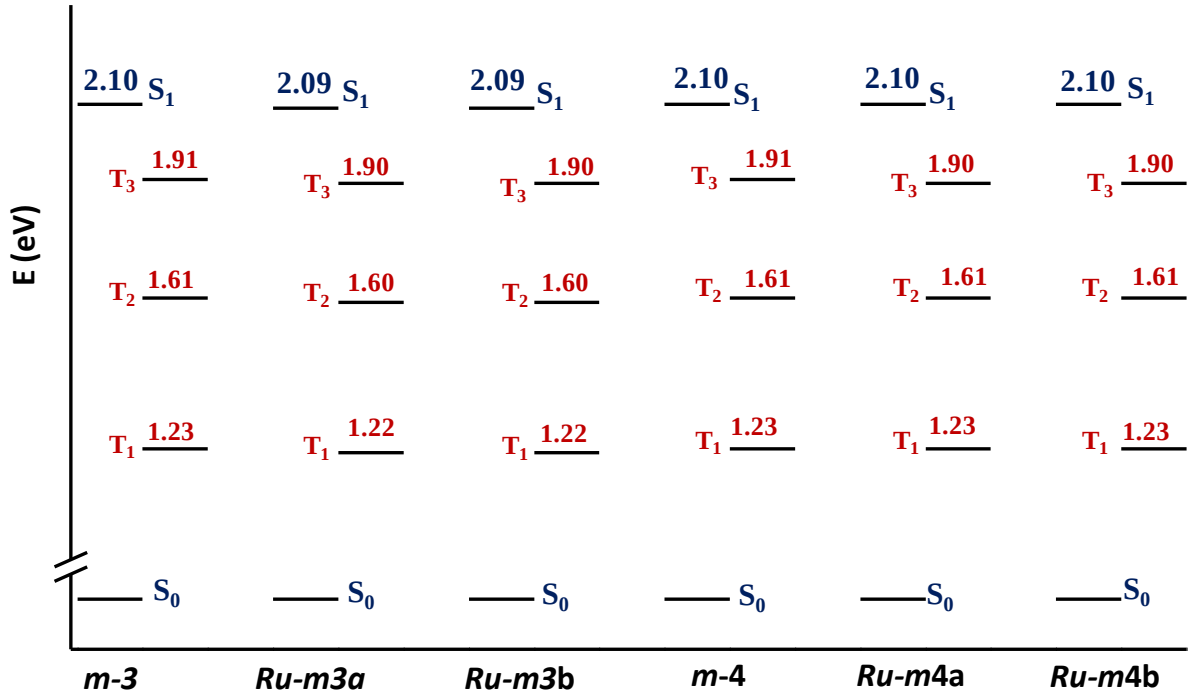
Compound	Soret Band	Q band IV	Q band III	Q band II	Q band I
Ru- ***m***3a[1]	**419**	515	**550**	589	**645**
Ru- ***m***3b[1]	**418**	515	**549**	589	**646**
m-4[2]	**415**	513	**547**	587	**644**
Ru- ***m***4a[1]	**418**	515	**551**	590	**646**
Ru- ***m***4b[1]	**419**	515	**551**	589	**645**

[1] J Biol Inorg Chem, 2009, 14, 101–109; **[2]** New J. Chem., 2000, 24, 555-560

Energy diagram and plots of the Gouterman orbitals for ***m*-3, Ru-*m*3a, Ru-*m*3b, *m*-4, Ru-*m*4a, Ru-*m*4b** compounds, calculated in water at M06/6-31+G(d,p)/SDD level of theory. H-L energy gaps are given in eV.

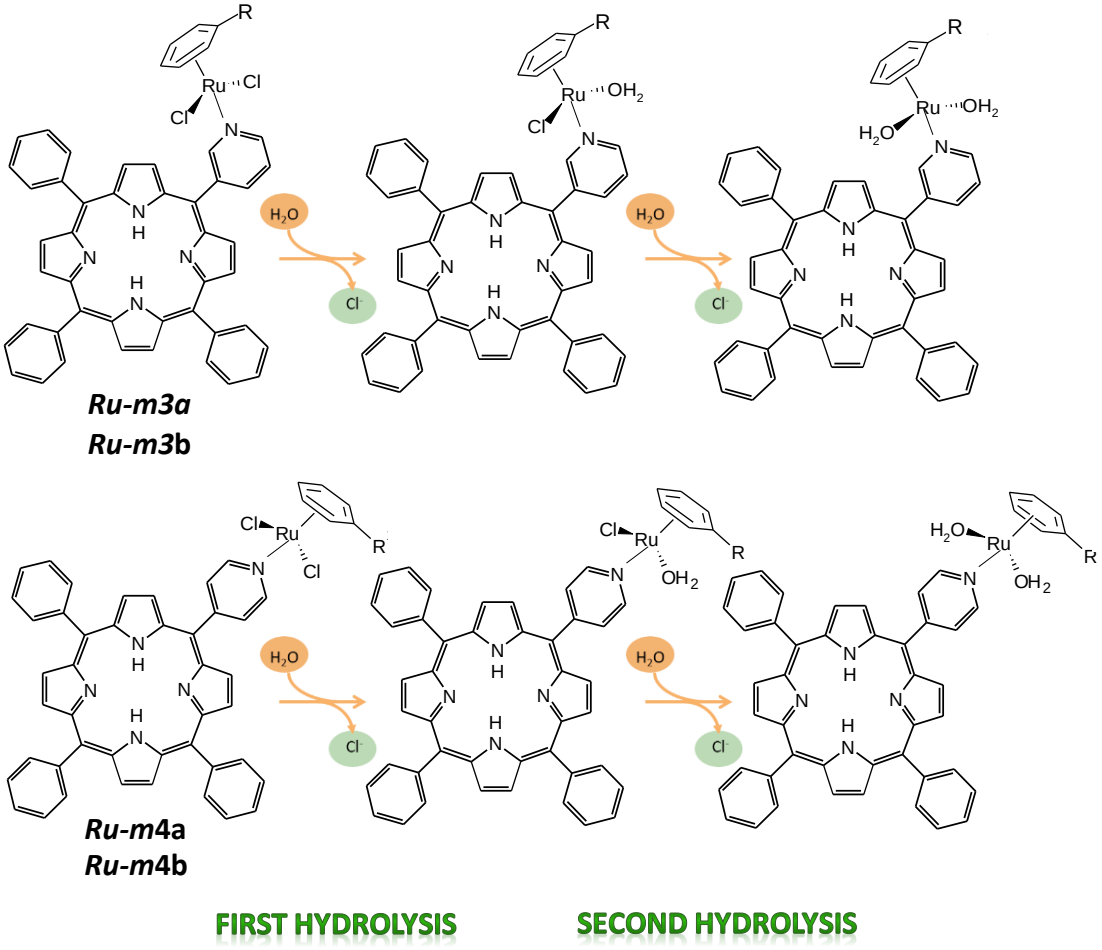


Lowest vertical singlet and triplet excitation energies (eV) for ***m*-3, Ru-*m*3a, Ru-*m*3b, *m*-4, Ru-*m*4a, Ru-*m*4b** computed in water at TD-M06/6-31+G(d,p)/SDD level of theory



a) Scheme of the studied Hydrolysis Processes and **b)** Computed activation free energies (kcal mol^{-1}), for first **I** and second **II** hydrolysis processes of **Ru-*m*3a, Ru-*m*3b, Ru-*m*4a, Ru-*m*4b** computed in water at B3LYP/6-31+G(d,p)/SDD//6-311++G(2df,2p) level of theory. To illustrate the reaction mechanism, the optimized structures intercepted along the hydrolysis free energy profiles are reported for **c) Ru-*m*3a** and **d) Ru-*m*4a** compounds.

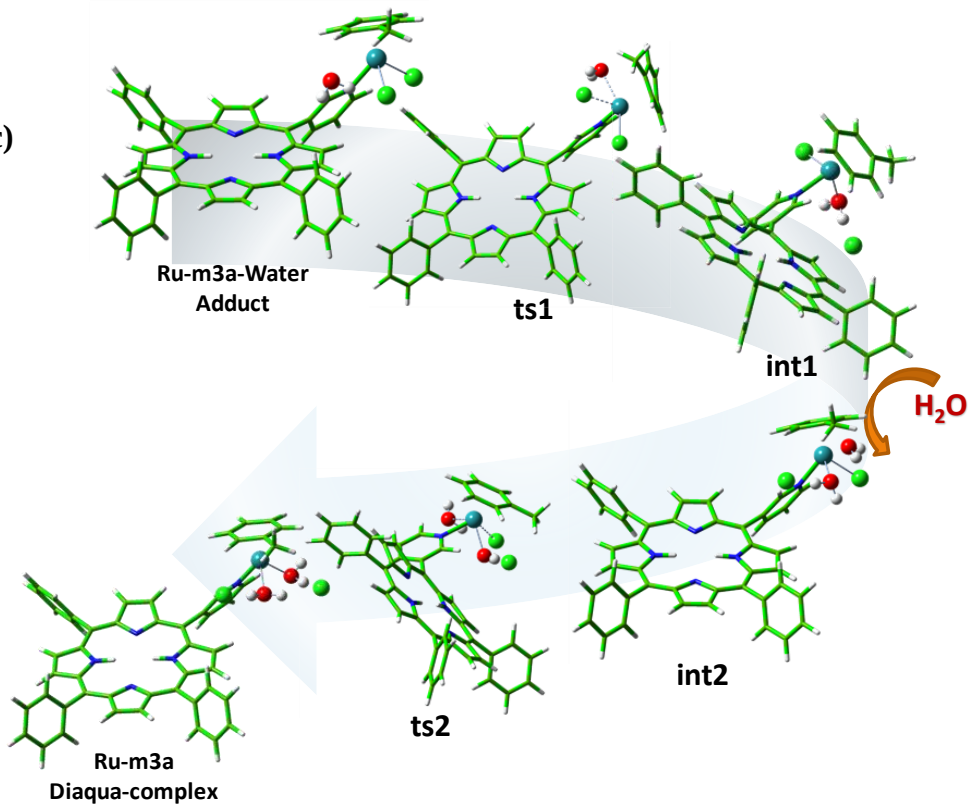
a)



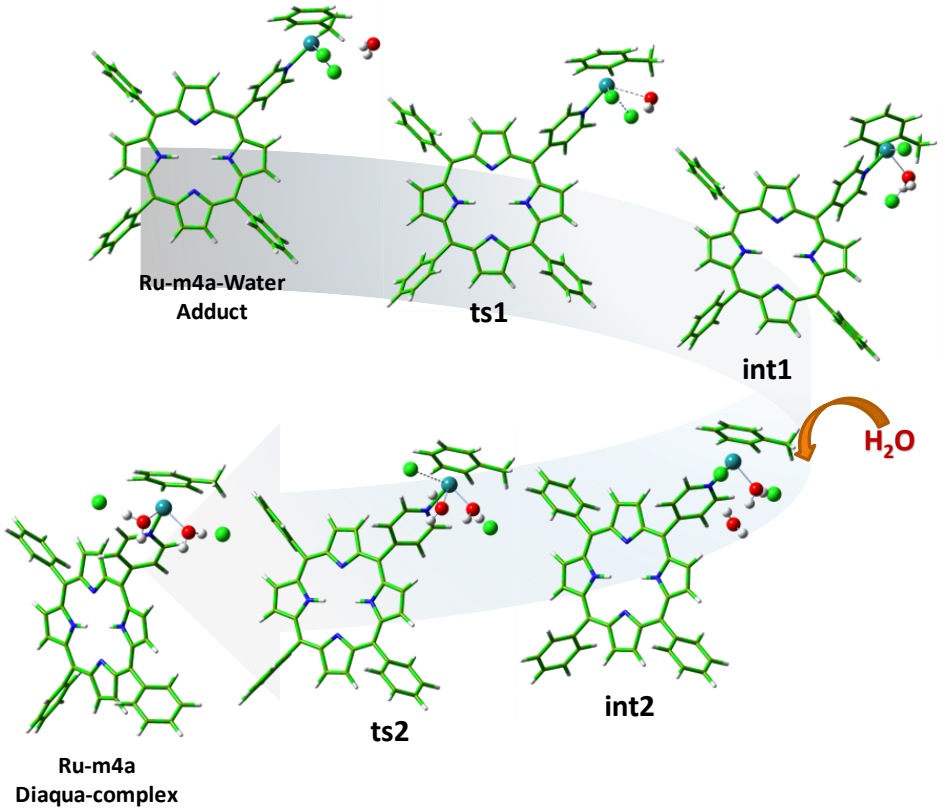
b)

Activation Free Energy (kcal/mol)		
	I Hydrolysis	**II Hydrolysis**
Ru-*m*3a	**24,8**	21,0
Ru-*m*3b	**20,4**	19,6
Ru-*m*4a	18,5	**24,0**
Ru-*m*4b	18,1	**24,0**

c)


Ru-m3a-Water
Adduct
ts1
int1
H_2O
int2
ts2
Ru-m3a
Diaqua-complex

d)


Ru-m4a-Water
Adduct
ts1
int1
H_2O
int2
ts2
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