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Research paper

Theoretical calculation of influence of halogen atoms (F, Cl, Br, I) on arylazopyridine (Azpy) ruthenium complexes behaving as photo sensitizers by DFT method

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Abstract

Photosensivity prediction of several azopyridine ruthenium complexes by DFT and TDDFT methods was performed. γ-RuX_2 (Azpy) $_2$ and δ-$RuX_2(Azpy)_2$ where X stands for F, Cl, Br and I were studied todetermine their activities when halide atoms shift. So, frontier orbital, NBO, NLMO and MLCT transitions as well as an excited lifetime of those complexes was determined. The main difference between them stems from both the electronegativity of the halide atoms and the structure of each complex. Hence, the rank of halide's electronegativity that is as follows$\chi_P(F)>\chi_P$ $(Cl)>\chi_P$ $(Br)>\chi_P$ (I) has been discovered to influence all the reactivity of the complexes regardless their structure. Herein, the comparison with the gap energy shows that the most reactive complexes are those with fluorine atom. Especially, δ-$RuF_2(Azpy)_2$ was admitted to be the most active isomer. Moreover, NBO calculation discloses that the complex becomes less ionic when the electronegativity decreases from F to I atoms. Furthermore, the calculation of NLMO orbitals shows that the bonding Ru-X are very strong. However, this strength decreases also from F to I and the nature of the bonding move from ionic to metallic. Moreover, the bonding from N_{py} and N_2 with Ru are known to be the same confirming the bidentate state of Azpy ligand. Regarding the electronic prediction, the eight complexes are surely assumed to display MLCT transitions that originate the photosensitivity. However, the complex that requires the least energy remains δ-$RuF_2(Azpy)_2$. This result was also determined by analyzing the excited lifetime that is the ability for a complex to longer linger in the cationic state. At last, we found out that with iodine atoms, the azopyridine ruthenium complex cannot behave as photosensitize dye insofar as I atom hides the main orbitals from Ru regardless the symmetry.

Keywords: *Azopyridine; Halide Atoms; NBO; NLMO; Ru(II) Complexes.*

1. Introduction

Since 1980, the ligand 2-Arylazopyridine complexing ruthenium atom is of great interest. It is used either as photo sensitizer to harvest electricity or as drug against cancer disease (Reedijk & Bouwman 1999, Reedijk 2003). It is also used as a catalyst to oxidize high-value molecules (Jorna et al. 1996). The advantage of exploiting this ligand is that it is bidentate (Affi et al. 2015). It is a π Acceptor and it reduces the state of oxidation of the metal to +II rendering it more selective. Thus, it binds metal remarkably well. Especially, $RuCl_2(Azpy)_2$ as has been the most exploited of all azopyridine complexes ever yielded up to day (Krause et al. 1980, Boa et al. 1988).

In this work, we intend to predict the optical asset and the reactivity of azopyridine ruthenium complex when the halide Cl is changed with F, Br or I as they all belong to the same halogen group in the periodic table, and they are assumed to display similar activity regardless their size. However, halide atoms can be slightly different from one another in a molecule owing to the difference of their inner shield electrons. For instance, several of their properties like the Pauling's electronegativity and the atomic radius that is assumed to be responsible for their reactivities varies respectively as follows:

$$\chi_P\ (F)=3.98>\chi_P(Cl)=3.16>\chi_P(Br)=2.96>\chi_P(I)=2.66$$

And

$$r\ (F)=1.17Å<r(Cl)=1.67Å<\ r(Br)=1.82Å<\ r(I)=2.06Å$$

Hence, while the electronegativity lowers in the group, the size enhances. Moreover, certain molecules can be toxic while other can be harmless (Shriver & Atkins 1999).

Besides, $RuBr_2$ (Azpy) $_2$ and RuI_2 (Azpy) $_2$ have experimentally been slightly studied. They are produced in the same way as $RuCl_2$ (Azpy) $_2$ by mixing up RuX_3, $3H_2O$ (X= Cl, Br and I) and Azpy ligand (Gowami et al. 1981, Krause & Krause 1982). Although it is reported that five isomers are expected for each complex owing to the asymmetry of the Azpy ligand, only two of them are hitherto produced by the following aforementioned process (Bamba et al. 2004, Velders et al. 2004) as displayed in Fig. 1.

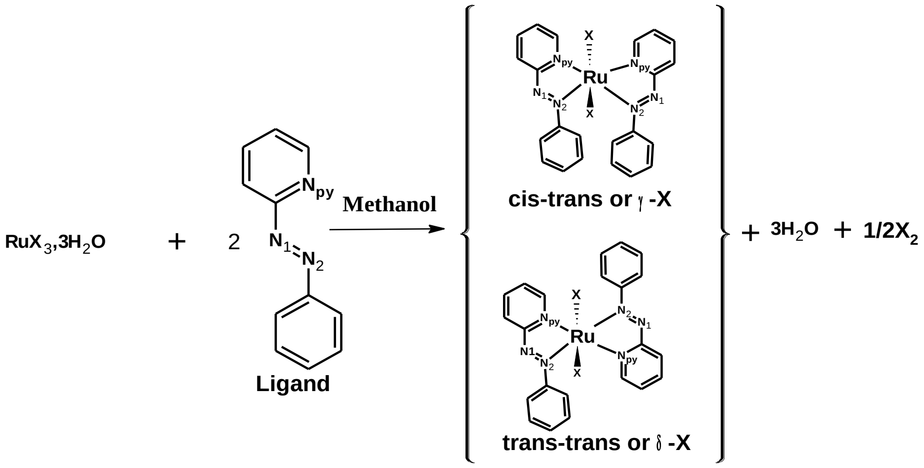

Fig.1: Synthesis of Azopyridine Ruthenium Complexes. in this Paper, X Stands for Halogen Atoms F, Cl, Br Or I. in Both Structures, Halogen Atoms are in Trans Position.

To best assure the explanation and the understanding of the subject, Fig. 2 displays the labeled ligand 2-phenylazopyridine (Azpy). It has been somewhat studied in our previous article (Affi et al. 2015, Bamba et al. 2016). Thus, we want to know of its mode of binding with the ruthenium when the halogen atoms are substituted.

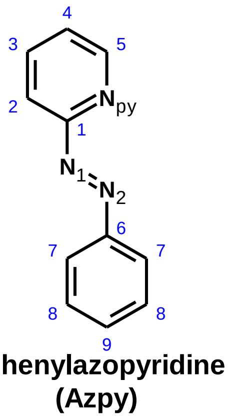

Fig.2: CommunAzopyridine Ligand Involved in the Formation of the Complexes Rux$_2$ (Azpy)$_2$, (X=F, Cl, Br or I). OnlyCarbon Atoms are numbered in Blue to Ease the Explanation of NLMO Theory. Thus, Those Numbers Are Different From That of Nitrogen Atoms in Azo Group Fragment.

2. Method

In this work, all calculations were undertaken with DFT method. In fact, the functional B3LYP was used with a separated basis set that comprises the pseudo-potential Lanl2dz exclusively for ruthenium and 6-31G (d) for the remaining atoms within the complex. This method is assumed to provide more accurate result consistent with experimental one. First, all molecules were optimized to find out the minimal energy that corresponds to the stationary point, then the frequency prediction was carried out to account for a lack of imaginary vibrational data. Regarding electronic prediction, it was carried out using the Time Dependent DFT (TDDFT) method with the same combined aforementioned basis set. Here, only absorption (vertical) energy is determined since it is admitted to be consistent with the experimental data (Adamo&Jacquemin 2013). Also, the Natural Bond Orbital NBO and the Natural Localized Molecular Orbital NLMO were used respectively to predict the atomic charge and to perform the mode of binding of the ligand to the ruthenium ion (Weinhold & Landis 2001), they were calculated thanks to the same separated basis set. In all the case, the whole calculations were performed using Gaussian 03 package (Frisch et al. 2003).

3. Results and discussion

3.1. Predicted geometrical parameters of the complexes

Table 1: Calculated Selected Bond Lengths (Å) and Angles Bond (Deg) of γ,δ-Rux$_2$(Azpy)$_2$ (X= F, Cl, Br and I)

Parameters	$RuF_2(Azpy)_2$		$RuCl_2(Azpy)_2$[a]		$RuBr_2(Azpy)_2$		$RuI_2(Azpy)_2$	
	γ-F	γ-F	γ-Cl	γ-Cl	γ-Br	γ-Br	γ-I	γ-I
Ru-X	1.99	2.04-1.99	2.45	2.48-2.46	2.58	2.61-2.60	2.82	2.83
Ru-N_2	1.99	2.04	2.04	2.07	2.04	2.06	2.05	2.07
Ru-N_{py}	2.16	2.10	2.13	2.12	2.13	2.12	2.13	2.11
N=N	1.29	1.28	1.28	1.27	1.28	1.27	1.28	1.28
X-Ru-X	173.74	180.00	171.40	180.00	170.67	180.00	170.16	180.00
X-Ru-N_2	90.99-92.92	89.76-90.24	90.33-94.86	89.77-90.23	90.61-95.00	89.74-90.26	91.09-94.82	87.16-92.84
X-Ru-N_{py}	81.73-94.54	81.66-98.34	85.30-89.41	83.69-95.31	85.61-88.66	85.60-94.40	86.57-87.38	89.49-90.51
N_2-Ru-N_2	102.66	179.52	105.83	178.58	105.95	179.48	106.18	180.00
N_2-Ru-N_{py}	75.36-174.21	75.46-104.61	75.04-179.10	75.18-104.87	74.99-178.86	75.09-104.95	74.96-178.17	74.82-105.18
N_{py}-Ru-N_{py}	107.13	163.32	104.08	167.53	104.08	171.19	103.95	180.00

[a]experiment data are taken from (Misra et al. 1997).

The main bonds and angles that characterize both metal and azopyridine ligand are displayed in Table 1. Regarding γ-X isomers, we can see that γ-RuF_2 (Azpy)$_2$ shows the shortest Ru-X bond with 1.99Å and the longest bond is given by γ-RuI_2 (Azpy)$_2$. The order of that Ru-X bond is presented as Ru-F (1.99Å) <Ru-Cl (2.45Å) <Ru-Br (2.58Å) <Ru-I (2.82Å). This result can be linked to the electronegativity of the halogen atoms in the periodic table in agreement with reference 3. Thus the high electronegativity will strengthen the Ru-X bond and thereby shortening its length. In consequence, a small shape of the molecule can be expected. Moreover, this same order was observed in the case of Ru-N_2 bond. However, regarding the Ru-N_{py} bond, except for γ-F whose bond length is 2.16Å, we can see that almost the remaining complexes display an invariable bonds with 2.13Å. Besides, γ-X isomers present only one data that characterizes each Ru-X bond length.

Which confirms a symmetry that allows each pair of atom to be in the same environment as we indicated in a previous paper (Nobel et al. 2017).Thus, those isomers are assumed to be C_2 symmetrical. For the angle bonds, we can see that X-Ru-X which value was set to 180° before calculation for each isomer was reduced according to the following rank: I-Ru-I (170.16°)< Br-Ru-Br(170.67°)< Cl-Ru-Cl(171.4°)< F-Ru-F(173.74°). Thus, the iodine atom reduces the angle more when the fluorine atom modifies it less. We can conclude furthermore that the shape of the halogen atom reduces the X-Ru-X angle bond within the molecule in the order (F< Cl< Br< I). Concerning the N_{py}-Ru-N_{py} angle bonds, they keep the same rank as X-Ru-X aforementioned. However, the N_2-Ru-N_2 bonds show the contrary rank. Anyway, we can admit that the size of cis-RuX_2 (Azpy)$_2$ increases from F to I atom in relation to their electronegativity and their atomic radius.

Regarding δ-X isomers where both azopyridine ligands are in trans position, the Ru-F, Ru-Cl and Ru-Br bonds are represented by two values thereby indicating that both halogen atoms are in different environment. Nevertheless, they are assumed to display a C_2 symmetry (Bamba et al. 2016). Yet, Ru-I displays one bond length. It shows up a center of symmetry. Therefore, it is a C_i symmetrical molecule. Besides, this structure was confirmed by its angle bonds regarding I-Ru-I, N_{py}-Ru-N_{py} and N_2-Ru-N_2 that values still remain 180° indicating that atoms in opposite positions through the Ru atom within the complex are identical by pair. Concerning Ru-X bonds, they increase from F to I however Ru-N bonds remain slightly the same. Herein, we can assume that electronegativity has no effect on Ru-N bonds. Anyhow, we can assume again that the shape of the complex increases from fluorine to iodine atoms regardless the structure of the isomer.

3.2. Electronic structures

3.2.1. Frontier molecular energy

Table 2: Energies (Kcal/Mol) of Frontier Orbitals with Gap Energy ΔE Calculated for Both γ- and δ-Rux_2 (Azpy)$_2$ Isomers

	$RuF_2(Azpy)_2$		$RuCl_2(Azpy)_2$		$RuBr_2(Azpy)_2$		$RuI_2(Azpy)_2$	
	γ-F	γ-F	γ-Cl	γ-Cl	γ-Br	γ-Br	γ-I	γ-I
HOMO (H)	-111.7	-105.65	-119.41	-116.03	-117.92	-114.66	-119.68	-117.25
LUMO (L)	-66.52	-67.41	-70.22	-71.72	-69.50	-71.34	-71.00	-72.99
NHOMO (H-1)	-119.33	-115.07	-126.24	-123.73	-123.33	-121.07	-123.51	-122.31
NLUMO (L+1)	-51.55	-51.43	-64.00	-63.40	-58.35	-55.74	-70.30	-69.00
ΔE^a	45.18	38.24	49.19	44.31	48.42	43.32	48.68	44.26
η	22.59	19.12	24.595	22.155	24.21	21.66	24.34	22.13
μ	-89.11	-86.53	-94.815	-93.875	-93.71	-93.00	-95.34	-95.12

Table 2 displays the frontier molecular orbitals and their relatives who comprise the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), the energy gap (ΔE), the chemical hardness (η) and the chemical potential (μ). As highlighted in our previous article (Bamba et al. 2016), they are assumed to define the reactivity of the molecule. The objective of our work therein was to see the state of the reactivity of the azopyridine ruthenium complex when only the modified parameter was the azopyridine ligand. Herewith, it resulted that the most reactive complex was δ-$RuCl_2$ (Azpy)$_2$ due to its shallow energy gap. Now, we need to modify the halogen parameter thereby keeping Azpy as azopyridine ligand and Ru as the metal center atomic. Actually, frontier orbitals provide two types of information: The first regards the internship reaction that stresses the reactivity of the molecule as formerly explained (Bamba et al. 2016). Therefore, the most active molecule is of course the one whose gap energy and hardness are very low. So, based on that analysis, we can assume that the most active molecule is still δ-X. More specifically, δ-RuF_2 (Azpy)$_2$is assumed to be the most active and the softest complex. The second information deals with reaction between two molecules. For instance, we consider the reaction between the azopyridine ruthenium complexes and DNA molecules insofar as the complex has been studied as a cytotoxic molecules. In this case, the complex is assumed to receive an electron from DNA molecule. In consequence, it must have a its low LUMO orbital higher than the HOMO orbital of the DNA. From this analysis, we can see that comparing both types of isomers, δ-X displays the lowest LUMO energy. Otherwise, δ-Xis the most active molecule to react with DNA.

3.2.2. NBO prediction

NBO analysis characterizes the electronic structure of each atom in the molecule. Hence, Table 3 displays the natural population of the ruthenium both in complex or as atomic. We can see here that the core electrons do not undergo any modification and are composed of 36 electrons. Regarding the valence orbital, the number of electron increases from fluorine atom to iodine atom. However, for Rydberg electrons, there are high for fluorine atom with 0.09 e^- and constant for other's atoms with 0.06 e^-. Consequently, the total electron population also increases from fluorine to iodine atoms. Therefore, the natural charge of the ruthenium slightly decreases. Through Table 3, we can see that the natural charge of ruthenium may depend only on the electronegativity of halogen atoms. To check this statement, Table 4 displays the natural charge of the main atoms involved in the bonding to the ruthenium atom. Here, we can see that the charge of the three nitrogen atoms both through the ligand isolated, and in the complexes is invariable. Therefore, it can be assumed that the ligand is not responsible for the natural charge of ruthenium. However, the charge of the halogen atoms alters according to their electronegativity regardless the isomer. Besides, we can see that in each *cis* (γ-X) isomer, the charge of both halogen atoms is the same confirming the C_2 symmetry of the complexes. Whereas the *trans* isomer, it displays different charge for both halogen atoms, although they are also C_2 symmetrical. Contrary for δRuI_2 (Azpy)$_2$, the complex is assumed to be C_i symmetrical. Therefore, it presents both iodine atoms with the same charge -0.45.

Table 3: Allotment of Electrons of Ruthenium as Ion when It Is Involved in the Complex or as Atom. This Distribution Is Made Between Core, Valence and Rydberg Orbitals

	CORE	VALENCE	RYDBERG	TOTAL	Charge Ru
γ$RuF_2(Azpy)_2$	35.99	7.05	0.09	43.13	0.87
δ$RuF_2(Azpy)_2$	35.99	7.08	0.09	43.16	0.84
γ$RuCl_2(Azpy)_2$	35.99	7.43	0.06	43.48	0.52
δ$RuCl_2(Azpy)_2$	35.99	7.45	0.06	43.50	0.50
γ$RuBr_2(Azpy)_2$	35.99	7.51	0.06	43.56	0.44
δ$RuBr_2(Azpy)_2$	35.99	7.52	0.06	43.57	0.43
γ$RuI_2(Azpy)_2$	35.99	7.62	0.06	43.67	0.33
δ$RuI_2(Azpy)_2$	35.99	7.62	0.06	43.67	0.33
Ru atom	36.00	8.00	0.00	44.00	0.00

Table 4: Charge of the Main Atoms Involved in Reaction in the Azopyridine Ruthenium Complex

	Isomer	Atoms					
		Ru	N_{py}	N_1	N_2	X	
$RuF_2(Azpy)_2$	Cis	0.87	-0.46	-0.24	-0.11	-0.59	-0.59
	Trans	0.84	-0.43	-0.21	-0.13	-0.60	-0.62
$RuCl_2(Azpy)_2$	Cis	0.52	-0.42	-0.22	-0.10	-0.54	-0.54
	Trans	0.50	-0.41	-0.19	-0.11	-0.55	-0.57
$RuBr_2(Azpy)_2$	Cis	0.44	-0.43	-0.21	-0.11	-0.49	-0.49
	Trans	0.43	-0.41	-0.19	-0.12	-0.50	-0.51
$RuI_2(Azpy)_2$	Cis	0.33	-0.44	-0.20	-0.12	-0.44	-0.44
	Trans	0.33	-0.42	-0.18	-0.13	-0.45	-0.45
Ligand Azpy			-0.44	-0.23	-0.15		

3.2.3. NLMO calculations

The natural localized molecular orbital (NLMO) tends to explain how bonding is performed between two atoms by displaying the molecular orbital (Reed et al. 1988). Table 5 shows the bondings that are set up for both isomers δ-X and γ-X while X stands for F, Cl, Br and I. The available atoms that are involved in the bondings are Ru, X, N_{py}, N_1 and N_2. We can see that two types of bonding are possible: the strong covalent bonding that is directly formed between two atoms and the weak bonding represented by a lone pair orbital whose molecular orbital highlights all atoms involved in the bonding. This last bonding is admitted to be a vanderwaals one. As we can notice, only halogen atoms actually perform strong covalent bonding with the ruthenium. The total number of electrons (indicated by NBO calculation) that each halogen atom shares with the ruthenium atom is almost the same confirming thereby the C_2 symmetry of both halide atoms. Moreover, we can assume that this high value regarding halogen atoms strengthens the theory arguing that the complex doesn't undergo any hydrolysis or substitution of halide atoms when binding to the DNA. So, the intercalation that is the most admitted theory for DNA to bind to the cytotoxic ruthenium complex must certainly be through the bonding with the ligand azpy (Chen et al. 2005). Moreover, as the C_2 symmetry means equality between opposite atoms through a C_2 axis by pairs, we can notice on table 3 a sort of compensation between the contribution of both atoms in performing each lone pair orbital. For instance, in γ-X isomers, both X atoms should be identical by displaying the same molecular orbital. Otherwise, if one of the halide is involved in a strong covalent bonding for example Ru-X_1 and the other is concerned by LP(X_2), then the first halide X_1 atom will contribute in the bonding of the second to Ru insofar as the molecular orbital of LP(X_2) shows up X_1 as a contributor. Therefore, both halide will present almost the same amount of occupancy.

Table 5: Nlmos Indicating the Mode of Bonding Between The Ruthenium and Main Atomics Involved in the Formation of Rux_2 (Azpy) $_2$with X= F, Cl, Br Or I. LP Means Lone Pair Orbital. It Is Admitted to Be the Main Donor of Electron to the Ruthenium Atom Thereby Forming A Weak Bonding. as the Complexes are Octahedral, the Bonding Is Performed Between Ru, X and N Atoms. Both Halide Atoms are Made Discernable by Numbers 1 and 2 to Better Understand the Theory

[a] LP means lone pair orbital;

NLMO	$RuF_2(Azpy)_2$			
		γ–X		δ–X
	Occupancies (%)	Molecular orbital	Occupancies (%)	Molecular orbital
LP(F_1)	98.43	σ= 82.52%(F_1)+15.91%(Ru)	98.78	σ= 79.62%(F_1)+19.17%(Ru)
LP(F_2)	98.44	σ= 82.51%(F_2)+15.93%(Ru)	98.69	σ= 84.60%(F_2)+11.37%(Ru)+2.72%(F_1)
LP(N_{py})	96.54	σ=85.53%(N_{py})+8.4%(Ru)+2.61%(N_2)	94.00	σ=83.15%(N_{py})+10.84%(Ru)
LP(N_1)	99.07	σ= 96.26%(N_1)+1.01%(C_1)+0.49%(N_{py})+0.41%(N_2)+0.9%(Ru)	99.19	σ= 96.71%(N_1)+0.92%(C_1)+0.44%(N_{py})+0.35%(N_2)+0.77%(Ru)
LP(N_2)	97.66	σ= 77.88%(N_2)+19.78%(Ru)	97.88	σ= 81.21%(N_2)+16.67%(Ru)
LP(Ru)	84.63	σ= 76.03%(Ru)+3.84%(N_1)+4.76%(N_2)	82.80	σ= 73.75%(Ru)+4.22%(N_1)+4.83%(N_2)
$RuCl_2(Azpy)_2$				
Ru-Cl_1	98.8	σ=72.90%(Cl_1)+25.90%(Ru)	98.66	σ=72.91%(Cl_1)+25.75%(Ru)
LP(Cl_2)	98.04	σ=78.02%(Cl_2)+14.88%(Ru)+5.14%(Cl_1)	98.17	σ=79.26%(Cl_2)+14.04%(Ru)+4.87%(Cl_1)
LP(N_{py})	96.97	σ=82.01%(N_{py})+11.72%(Ru)+3.24%(N_2)	96.4	σ=83.10%(N_{py})+11.35%(Ru)+1.95%(N_2)
LP(N_1)	99.13	σ= 96.51%(N_1)+0.91%(C_1)+0.46%(N_{py})+0.35%(N_2)+0.9%(Ru)	99.22	σ= 96.80%(N_1)+0.86%(C_1)+0.40%(N_{py})+0.35%(N_2)+0.81%(Ru)
LP(N_2)	97.77	σ= 79.76%(N_2)+15.20%(Ru)+2.81%(N_{py})	97.08	σ= 81.07%(N_2)+16.01%(Ru)
LP(Ru)	87.00	σ= 80.42%(Ru)+2.66%(N_1)+3.91%(N_2)	87.07	σ= 79.80%(Ru)+3.16%(N_1)+4.11%(N_2)
$RuBr_2(Azpy)_2$				
Ru-Br_1	98.37	σ=69.42%(Br_1)+28.95%(Ru)	97.91	σ=68.27%(Br_1)+29.64%(Ru)
LP(Br_2)	97.12	σ=75.58%(Br_2)+15.36%(Ru)+6.18%(Br_1)	97.07	σ=76.00%Br_2)+14.72%(Ru)+6.35%(Br_1)
LP(N_{py})	96.95	σ=82.10%(N_{py})+11.66%(Ru)+3.19%(N_2)	96.38	σ=81.34%(N_{py})+15.04%(Ru)
LP(N_1)	99.13	σ= 96.51%(N_1)+0.91%(C_1)+0.45%(N_{py})+0.35%(N_2)+0.91%(Ru)	99.22	σ= 96.82%(N_1)+0.84%(C_1)+0.40%(N_{py})+0.32%(N_2)+0.84%(Ru)
LP(N_2)	97.77	σ= 77.30%(N_2)+20.47%(Ru)	96.19	σ= 82.54%(N_2)+11.64%(Ru)+2.05%(N_{py})
LP(Ru)	87.15	σ= 80.67%(Ru)+2.62%(N_1)+3.86%(N_2)	87.11	σ= 79.76%(Ru)+3.46%(N_1)+3.89%(N_2)
$RuI_2(Azpy)_2$				
Ru-I_1	97.89	σ=65.05%(I_1)+32.84%(Ru)	97.70	σ=65.88%(I_1)+31.84%(Ru)
LP(I_2)	95.93	σ=72.64%(I_2)+15.73%(Ru)+7.56%(I_1)	95.86	σ=73.11%(I_2)+15.49%(Ru)+7.26%(I_1)
LP(N_{py})	96.96	σ=82.30%(N_{py})+11.58%(Ru)+3.08%(N_2)	95.45	σ=83.04%(N_{py})+11.41%(Ru)+1%(N_2)
LP(N_1)	99.15	σ= 96.51%(N_1)+0.90%(C_1)+0.44%(N_{py})+0.35%(N_2)+0.95%(Ru)	99.23	σ= 96.78%(N_1)+0.84%(C_1)+0.40%(N_{py})+0.34%(N_2)+0.87%(Ru)
LP(N_2)	97.72	σ= 80.29%(N_2)+14.76%(Ru)+2.67%(N_{py})	96.94	σ= 81.13%(N_2)+15.81%(Ru)
LP(Ru)	87.76	σ= 81.90%(Ru)+2.36%(N_1)+3.50%(N_2)	87.30	σ= 80.06%(Ru)+3.43%(N_1)+3.81%(N_2)

[a] LP means lone pair orbital;

Regarding the RuF$_2$ (Azpy)$_2$, all the bondings in both types of isomers are carried out through the lone pair of halide or nitrogen atoms. Both halide atoms show almost the identical molecular orbital where the bonding is assumed to be performed mainly between the halide and the ruthenium atoms, i.e., LP (F$_1$) = LP (F$_2$). Besides in the *trans* (δ-F) isomer, we can see that LP(F$_2$) is compensated by F$_1$ to balance out both lone pair orbitals so as to keep the same number of electron in each bonding. Concerning LP (N$_{py}$) and LP (N$_2$) that are expected to bind to ruthenium atom through weak covalent bondings, both also show the same number of electron with some natural compensation. This result from NLMO theory one more confirms the bidentate state of the azopyridine ligand as demonstrated before (Affi et al. 2015). Whereas LP (Ru), it shows that electrons from ruthenium are delocalized in the azo bonding N$_1$=N$_2$ emphasizing the metal to ligand charge transfer MLCT transition as explained in the previous article (Nobel et al. 2015). Regarding LP(N$_1$), its occupancies are so high (1.96 e) that it nearly delocalizes them either in C$_1$-N$_{py}$ bonding or in N$_2$ atom or remotely in Ru atom indicating that N$_1$ is not allowed to bind to Ru atom.

Similarly in both isomers of RuCl$_2$ (Azpy)$_2$, we can see that Ru-Cl$_1$ and LP (Cl$_2$) have the same number of electrons. Also, the molecular orbital of LP (Cl$_2$) is made of atomics orbitals of Cl$_2$, Ru and Cl$_1$ so as to get the same occupancies with Ru-Cl$_1$ bonding. Furthermore, LP (N$_{py}$) and LP (N$_2$) display also the same number of electrons (1.62 e) and their MOs show the bonding respectively between N$_{py}$ and N$_2$ with Ru. Regarding LP (Ru), it delocalizes its occupancies in the azo bond similarly to RuF$_2$ (Azpy)$_2$.

When we consider RuBr$_2$ (Azpy)$_2$, both isomers indicate Ru-Br$_1$ and LP(Br$_2$) as strong bonds between Ru and Br atoms since they display an equal number of electron. Moreover, Ru-Br$_2$ is compensated by Br$_1$ to have a C$_2$ symmetry. The same remark is made with both LP (N$_{py}$) and LP (N$_2$) where we have almost the same distribution of occupancies. Whereas LP (N$_1$) and LP (Ru), they show respectively that N$_1$ doesn't intervene in binding with ruthenium and Ru delocalizes in azo bond.

Regarding at last RuI$_2$ (Azpy)$_2$, it indicates the same observations as in RuBr$_2$ (Azpy)$_2$. Anyhow, we can see that from F to I, the strength of Ru-X lowers as the contribution of the halide wanes. Therefore, the nature of Ru-X moves slightly from ionic covalent bonding to a simple metallic bonding since the coefficient of the Ru metal increases.

3.2.4. TDDFT vertical excitation energies ΔE (eV)

Table 6: Frontier Orbitals with Their Compositions (%), Vertical Energy (Ev) of the Maximum Wavelength (Nm) with the Frequency, the Excited Lifetime τ(Ns) and the Main Transition Regarding Each Energy

Complexes	composition of FrontierOrbitals		ΔE(eV)	λ_{max}(nm)	f	τ(ns)	Main transition
	HOMO	LUMO					
γ-RuF$_2$(Azpy)$_2$	Ru(55%) F(17%)	Azpy (82%)	1.73	715.14	0.086	89.14	H→L+2 (54%)
			2.27	547.02	0.099	45.31	H-2→L (65%)
			2.88	429.94	0.147	18.85	H-3→L(63%)
δ-RuF$_2$(Azpy)$_2$	Ru(66%) F(19%)	Azpy (92%)	1.48	838.48	0.084	125.46	H-1→L (70%)
			2.41	514.68	0.02	198.54	H-2→L+1 (60%)
			2.71	456.66	0.082	38.12	H→L+2 (57%)
γ-RuCl$_2$(Azpy)$_2$	Ru (55%) Cl(33%)	Azpy (86%)	1.78	697.7	0.052	140.33	H→L+1 (48%)
			2,15	577.8	0.066	75.83	H-2→L (65%)
			2.83	438.2	0.153	18.81	H-3→L (62%)
δ-RuCl$_2$(Azpy)$_2$	Ru (61%) Cl(32%)	Azpy (93%)	1.61	768.7	0.061	145.21	H-1→L (70%)
			2.32	533.5	0.012	355.54	H-2→L+1 (68%)
γ-RuBr$_2$(Azpy)$_2$	Ru (47%) Br(42%)	Azpy (85%)	1.73	718.01	0.047	164.42	H→L+1 (54%)
			2.12	584.68	0.038	134.85	H-2→L (51%)
δ-RuBr$_2$(Azpy)$_2$	Ru (53%) Br(40%)	Azpy (92%)	1.5	823.91	0.042	242.28	H-1→ L (70%)
γ-RuI$_2$(Azpy)$_2$	Ru (44%) I(46%)	Azpy (85%)	1.73	718.56	0.0317	244.16	H→L+1 (61%)
			2.12	585.85	0.01	514.49	H-3→L (58%)
δ-RuI$_2$(Azpy)$_2$	Ru (51%) I(44%)	Azpy (92%)	1.47	841.69	0.023	461.72	H-1→ L (70%)
			3.11	399.14	0.111	21.51	H→L +2 (58%)
RuCl$_3$,3H$_2$O	Ru (60%) Cl(38%)	Ru (70%)	2	516.8	0.061	65.63	H-2→L (98%)

The TDDFT calculations were performed to know of the transition states that the complexes can provide to behave as photochemical dye when they are excited. Table 6 displays the compositions of frontiers orbitals with the vertical energy required for the maximum wavelength of each transition. The main transition means here that for the same vertical energy, many transitions can be possible. Which is consistent with delocalization character of electron. Moreover, Table 7 presents the composition of molecular orbital from Homo (H) to H-3 and from LUMO (L) to L+3 for each ruthenium complex. All those orbitals can actually be involved in electronic transitions. We notice that HOMO (H) and next HOMO (H-1) orbitals are principally made of atomic orbital of both Ru and halide atoms. We can also see that the involvement of the halide atoms increases from fluorine to iodine while the contribution of Ru collapses. However, H-2 is exclusively made of ruthenium atomic orbital except in Ru-I complexes where AO from iodine atom governs the molecular orbital. At last, H-3 is dominated by orbitals of halide atoms except in complexes δ-Ru-F and γ-Ru-Cl where the main contributor is azpy ligand. Regarding the group of LUMO orbitals, we can see that from L to L+3, orbital is made of Azpy ligand in almost all the complexes except for Ru-I where I is more involved as main contributor. Furthermore, both γ-Ru-I and δ-Ru-I have the same diagram of orbital as confirmed in Table 5 with NLMO prediction.

Actually, the complex is considered as sensitizer if during the excitation, electron is thrown out of the metal. Hence, transitions must originate from metal orbital. Besides, the excited energy in Table 3 for each transition corresponds to energy necessary for its allowance. The lowest energy induces a more active complex. According to this analysis, we can assume that the most active complexes hitherto are δ-X isomers. Moreover, all their transitions are metal to ligand charge transfer (MLCT) types. Again, we can see in γ-X complexes some transitions originated from ligand. Those transitions like H-3→L are admitted to be LLCT type. Their vertical energy are high thereby reducing their sensitivity. Furthermore, we can see through iodine atoms in both isomers that orbital from ruthenium are hidden. Therefore, to have an MLCT transition, much excited energy must be required. Consequently, we can assume that I atom hampers azopyridine complexes from behaving as a photosensitizer certainly owing to its big size. In summary, δ-Ru-F isomer is assumed to be the most sensitive complex to excite semi-conductor to harvest electricity.

Moreover, the excited lifetime characterizes also a strength of complex to behave as a sensitizer (Chaofan et al. 2016). It is defined as $\tau(s) = \frac{1.499}{f\sigma^2}$ where f is the frequency and $\boldsymbol{\sigma}$ corresponds to the wavenumber (cm^{-1}) necessary to allow the excitation. It also corresponds to time that a complex lasts to stay in its excited state. Hence, the high lifetime will engender the more sensitizer complex. Table 6 displays the excited lifetimes of transition states. By comparing those coming from MLTC transitions according to both Tables 6 and 7, we discover that the most sensitive complex is δ-RuF_2 (Azpy)$_2$ with a vertical energy of 1.48 eV and an excited lifetime of 125.46 ns.

Table 7: Compositions (%) of Several Molecular Orbitals Comprising Frontiers Orbitals of γand δ-Rux_2 (Azpy)$_2$ Complexes. Bold Data Show the Main Contributor Atom or Molecule in Performing the Molecular Orbital

	$RuF_2(Azpy)_2$						$RuCl_2(Azpy)_2$						$RuBr_2(Azpy)_2$						$RuI_2(Azpy)_2$					
	γ-F			δ-F			γ-Cl			δ-Cl			γ-Br			δ-Br			γ-I			δ-I		
	Ru	F	Az-py	Ru	F	Az-py	Ru	Cl	Az-py	Ru	Cl	Az-py	Ru	Br	Az-py	Ru	Br	Az-py	Ru	I	Az-py	Ru	I	Az-py
HOMO (H)	55	17	28	66	19	15	55	33	12	61	32	7	47	42	11	53	40	7	44	46	9	51	44	5
NHOMO (H-1)	51	25	24	45	24	31	40	47	13	40	46	15	31	59	10	31	57	12	25	67	8	27	64	9
H-2	82	1	17	82	0	18	82	3	15	86	0	14	34	56	10	86	0	14	2	87	10	2	86	12
H-3	1	4	95	1	6	93	1	17	82	1	77	22	3	85	13	2	83	15	4	87	8	2	91	7
LUMO (L)	14	4	82	7	1	92	8	6	86	3	4	93	8	7	85	2	6	92	7	8	85	1	7	92
NLUMO (L+1)	23	2	75	25	2	73	19	1	80	20	1	79	19	1	80	20	1	80	18	0	82	20	0	80
L+2	4	0	96	2	0	98	4	0	96	2	0	98	4	0	96	2	0	98	49	36	15	49	36	15
L+3	3	0	97	5	0	95	3	0	97	4	0	96	3	1	96	4	0	96	4	1	95	2	0	98

4. Conclusion

In this work, we were comparing efficiency of azopyridine ruthenium complexes as photosensitizers when halide atoms were replaced with DFT and TDDFT methods. First of all, the geometry was predicted and we discovered that the size of the complex depends on the halide atom's electronegativity. Then, the most eletronegative atom that is F reduces the size of the complex. Regarding the electronic calculation, NBO and NLMO reveal that the more negative halide atom cancels the positive charge of Ru ion in the complex and confirm the bidentate state of ligand Azpy by displaying the same number of electrons for both LP(N_{py}) and LP(N_2) atoms. They show also that the strength of Ru-X reduces when the electronegativity decreases. Whereas the TDDFT prediction, it shows up that all the complexes display an MLCT transition. But their occurrences require more excited energy when we go from F to I in the periodic table. Hence, RuI_2 (Azpy)$_2$ cannot be used as photosensitizer as its metallic orbitals are actually hidden by the big size of the iodine atom. Whereas the δ-$RuF_2(Azpy)_2$, it is admitted to be the most sensitive molecule insofar as its metallic orbital requires the least energy to liberate electron through MLCT transition and its excited lifetime is high to maintain it in cationic shape. This result was confirmed by the frontier orbitals prediction.

Now, regarding the coming prediction, we need to replace the ruthenium atom by other atoms in same group of the periodic table. Therein, we will find out the most sensitive complex that is need to be synthesized and to be experienced.

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