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Theoretical Characteristics of Metalloporphyrins (OEP) M (CH_3) (M=Al, Ga, In and Tl)

Lepetit MB[1], Kabbaj OK[2], Zrineh A[3]

[1]*Institut Néel, CNRS UPR 2840, Grenoble, Institut Laue Langevin, Grenoble, France*
[2]*Department of Laboratory of Spectroscopy, Molecular Modeling, Materials and Environment, LS3ME, University Mohammed V, Rabat, Morocco*
[3]*Department Laboratory of Physical Chemistry of Materials, Nanomaterials and Environment, University Mohammed V, Rabat, Morocco*

ABSTRACT

A theoretical study of metalloporphyrins molecules (OEP) M (CH_3) (M=Al, Ga, In and Tl) are brought to a few experimental data and to give background for future development of these complexes. The Quantum Chemistry Program (ORCA) program package based on Density Functional Theory (DFT) and Time-dependent Density Functional Theory (TDDFT) for transitions at the B3LYP level with ANO 2ζ+P base was used for calculations and determination of structural properties, electronic properties and orbitals with associated electronic transitions. A structural, energy and orbital analysis was performed to study the interactions between metal and porphyrinic macrocycle, to establish different electronic transitions to understand the influence of the metal's nature. The results obtained are in good accord with some previous theoretical results and experimental investigations.

Keywords: Quantum chemical calculations, Density Functional Theory (DFT), Quantum Chemistry Program (ORCA), Metalloporphyrins complexes

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INTRODUCTION

Porphyrins are an important class of molecules because of their unique electronic properties. Even if porphyrins have been the subject of intense studies for several decades, they remain a very active domain as witnessed by the recent elaboration by R. Ruppert of new architectures for the base porphyrins complexes [1].

Porphyrins are organic molecules that perform as macrocyclic ligands. They contain four pyrol rings connected by methine bridges that can form complexes with different metal atoms, through their four nitrogen lone pairs. The metalloporphyrins have been the subject of numerous experimental studies for their biological [2-5] as well as medicine, agronomy, microelectronics, optoelectronics, catalysis [6,7] and biotechnology applications [8-10]. As a consequence numerous metal-carbon and metal-metal bonded metalloporphyrins such as the (OEP)M(CH_3) [11-14] and (OEP)M($ReCO_5$) [15] have been synthesized. The Octaethylporphyrins (OEP) are characterized by eight ethyl ligands bonded to the β carbons of the pyrrole groups (Figure 1).

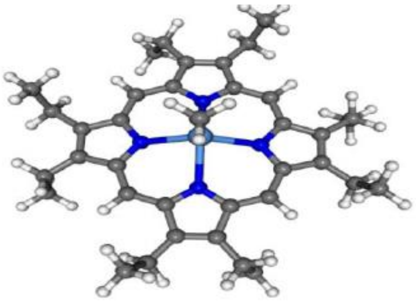

Figure 1: Schematic picture of (OEP)M(CH_3). Carbons are in black, hydrogen's in white, nitrogen's in dark blue and the metal in light blue

Because of their conjugated electronic structure, porphyrins are colorful. They absorb in the range of the visible-light wavelengths as well as in the near UV range and their spectra present very characteristic features. There is an intense peak between 390 and 430 nm called the "Soret band" and several bands of much lower intensity located between 480 and 700 nm, called the "Q bands" [16]. The latters are sensitive to structural variations and to the system environment. Such modifications induce shift in their positioning and modifications of their relative intensities. Their number can generally distinguish between free bases porphyrins from metalloporphyrins, respectively 4 or 2.

It is shown that the aluminum and gallium complexes are less stable than the indium and thallium ones [17]. In this work we will theoretically study the structural and spectroscopic properties of the group 13 MCH_3 octaethylporphyrin metalloporphyrin in gas phase. Indeed, Density Functional Theory (DFT) and Time-dependant Density Functional Theory (TDDFT) calculation provide a useful tool to access to gaz phase geometrical information as well as the nature of the different transitions; both type of information's difficult to access by experimental means. Indeed, while experimentally there are numerous studies (^{1}H NMR, UV-Visible and IR) [11-14] on these systems, little has been done yet on the theoretical level.

MATERIALS AND METHODS

The present work presents DFT [18] and TDDFT [19] calculations done using the ORCA software package [20,21]. The calculations were performed using the B3LYP functional [22-25] associated with an ANO 2ζ+P atomic basis set built in the ORCA code (BNANO_DZP) [26]. In addition, the core electrons of the heavy atoms (Ga, In, Tl) were treated using a small-core Stuttgart-Koeln effective potential [27,28]. The particle-hole nature of the different electronic excitations is studied using the transition natural orbitals, Eigen values of the transition density matrices of each excitation.

RESULTS AND DISCUSSION

Geometry

We performed full geometry optimization without any symmetry restrictions for the four metal atoms of column 13.

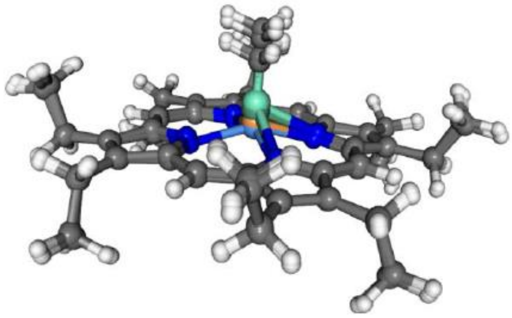

Figure 2: Optimized geometries for the Al (blue), Ga (orange), In (green), Tl (light green) (OEP)M(CH_3)

The octaethylporphyrin is a highly conjugated planar molecule, except for the external eight ethyl groups. Our calculations show that the OEP geometry is essentially unaffected by the MCH_3 complexation and the nature of the metal atom (Figure 2). Indeed, its D_{4h} symmetry is nearly preserved despite the presence of the methyl group; there is no rotation around the free axes of the ethyl ligands for any of the metals; the only influence of the MCH_3 group is a slight pyramidalisation of the OEP that increases with heavier metal atoms. The distance between the OEP nitrogens and the metals increases from aluminium to thallium as expected from the increase of their ionic radii. One can see on Table 1 that the metal-average porphyrin ring distance (Δ) behaves in a similar manner. The metal-methyl distance behaves however differently. Indeed, it presents two groups: Al and Ga with a distance of 2 Å, In and Tl with a distance of 2.2 Å. These geometries are in good agreement with the experimental crystal structures (Table 1: Δ is the distance between the average plane of the porphyrin and the metal. In parenthesis are the experimental values for crystalline similar compounds: (OEP) $AlCH_3$ [11], (TPP) In CH_3 [29], (TPP) $TlCH_3$ [30].

Table 1: Main distances of the (OEP) M(CH_3) complexes

	Δ (Å)	M - N (Å)	M - C (Å)
(OEP)$AlCH_3$	0.50 (0.47)	2.07 (2.03)	1.99 (1.94)
(OEP)$GaCH_3$	0.59	2.12	2
(OEP)$InCH_3$	0.83 (0.78)	2.24 (2.21)	2.19 (2.13)
(OEP)$TlCH_3$	1.02 (0.98)	2.33 (2.29)	2.22 (2.15)

Charges

The Mulliken's charge analysis is reported in Table 2. One sees that the partial charges on the four nitrogen atoms are equivalent (pseudo 4-fold axis) and not affected by the nature of the metal atom. On the contrary the metal charges differ from one metal to the other, going from 0.6 for Al to 0.8 for In. The differential electronic population is equally spread over the porphyrinic ring. The metals Mulliken charges varies similarly to the atoms Pauling electro negativities (Al: 1.61, Ga: 1.81, In: 1.78, Tl: 2.04), except for the Ga.

Table 2: Mulliken charges of the (OEP) M (CH3) complexes

	Mulliken charges				
	N_1	N_2	N_3	N_4	M^{3+}
(OEP)$AlCH_3$	-0.36	-0.36	-0.36	-0.36	0.59
(OEP)$GaCH_3$	-0.34	-0.34	-0.34	-0.34	0.62
(OEP)$InCH_3$	-0.37	-0.37	-0.37	-0.37	0.82
(OEP)$TlCH_3$	-0.35	-0.35	-0.35	-0.35	0.75

Frontier molecular orbitals

The (OEP)Al(CH_3) and (OEP)Ga(CH_3) do not have any electrons at the Fermi level, namely, the HOMO and the quasi degenerated LUMO and $LUMO^{+1}$ orbitals ($\Delta E_{LUMO/LUMO+1}$ ~0.1 meV for all compounds) correspond to the HOMO and LUMO orbitals of the free-based prophyrin and do not exhibit any weight on the MCH_3 part (Figure 3).

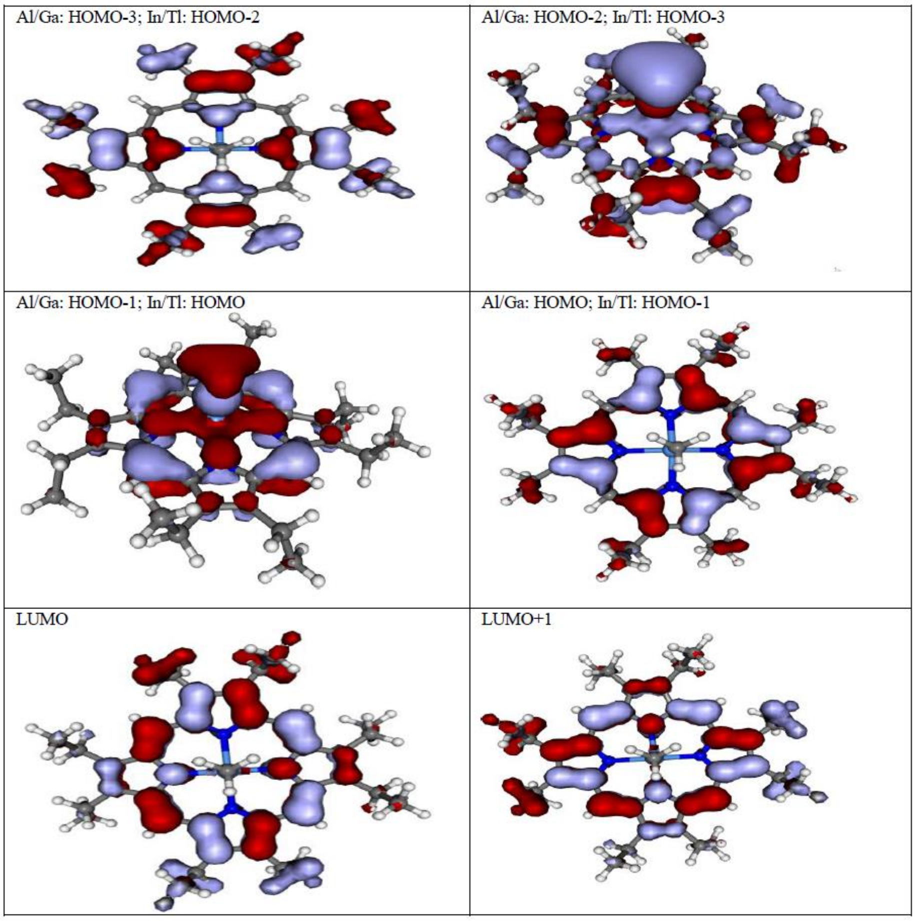

Figure 3: Schematic representation of the frontier orbitals for the (OEP)M(CH_3)

Instead, the HOMO orbitals of the In and Tl compounds present a strong contribution of the MCH_3, the two LUMOs orbitals being similar to the Al and Ga compounds. The HOMO, HOMO-1 and LUMOs orbital of the four compounds do well correspond to the four frontier orbitals defined in the Gouterman model [31].

What is striking is that despite this fact the HOMO-LUMO gap remains nearly unchanged. In fact there is a crossing between the energy levels of the HOMO and HOMO-1 of the Al/Ga systems and the In/Tl ones. One should however notice that for all compounds the HOMO/HOMO-1 orbitals have very close energies. One can see in Table 3 that the gap between the orbitals without contributions of the MCH_3 remains constant (bold numbers in Table 3), while the gap between the LUMO and the occupied orbital containing a MCH_3 character very slightly decreases with increasing metal atomic number. It is noticeable that the latter exhibits a weight on the metal dz^2 orbital for Ga, In and Tl but not for Al. This is probably due to the more localized character of the 3d orbitals.

A similar closeness in energy appears between the HOMO-2 and HOMO-3 for all compounds. As for the HOMO, HOMO-1, the HOMO-2 and HOMO-3 are exchanged between the Al/Ga and the In/Tl systems.

These exchanges are related to the metal OEP-pyrrol interactions. Indeed, the d_{x2-y2} orbital of the metal is strongly delocalized on the σsp^2 lone pair of the pyrrol nitrogen. This delocalized orbital is bonded with the carbons of the pyrol ring in the HOMO-2 (resp.3) orbitals, while it is antibonded in the HOMO-1 (resp. HOMO) orbitals (Table 4). When the metal goes from Al to Tl, this metal-pyrrol interaction increases due to the larger size of the metal nd orbitals and as a consequence, the hopping integral. It classically results, in an energy lowering for the less energetic orbital and an energy increase for the higher energy one.

Table 3: Frontier orbitals energies differences (in eV)

Metal	$\Delta E_{LUMO/HOMO}$	$\Delta E_{LUMO/HOMO-1}$	$\Delta E_{LUMO/HOMO-2}$	$\Delta E_{LUMO/HOMO-3}$
Al	2.90	2.94	3.90	4.08
Ga	2.91	2.92	4.04	4.07
In	2.90	2.91	4.02	4.02
Tl	2.88	2.91	3.99	4.10

Table 4: Orbital content

Metal	HOMO	HOMO-1	HOMO-2	HOMO-3
Al	OEP (A_{1u})	Bridge OEP (A_{2u}) + p_z(Al)+d_{x2-y2}(Al)+CH3	Pyrrol OEP (A_{2u}) + d_{x2-y2}(Al)+CH3	Pyrrol OEP (A_{2u})
Ga	OEP (A_{1u})	Bridge OEP (A_{2u}) + p_z(Ga)+d_{z2}(Ga)+CH3	Pyrrol OEP (A_{2u}) + p_z(Ga)+CH3	Pyrrol OEP (A_{2u})
In	Bridge OEP (A_{2u}) + p_z(In)+d_{x2-y2}(In)+CH3	OEP (A_{1u})	Pyrrol OEP (A_{2u})	Pyrrol OEP (A_{2u}) + p_z(In)+d_{x2-y2}(In)+CH3
Tl	Bridge OEP (A_{2u}) + p_z(Tl)+d_{z2}(Tl)+CH3	OEP (A_{1u})	Pyrrol OEP (A_{2u})	Pyrrol OEP (A_{2u}) + p_z(Tl)+d_{z2-}(Tl)+CH3

Electronic excitation spectra

We computed the electronic excitation spectra using the TDDFT method within the ORCA package from the Fermi level up to about 48000 cm^{-1}. Figure 4 displays the absorption spectra computed using a Gaussian line shape and a 1500 cm^{-1} line width. One can see that the total absorption spectra for the four complexes are very similar, the lines being either red shifted or blue shifted according to their nature.

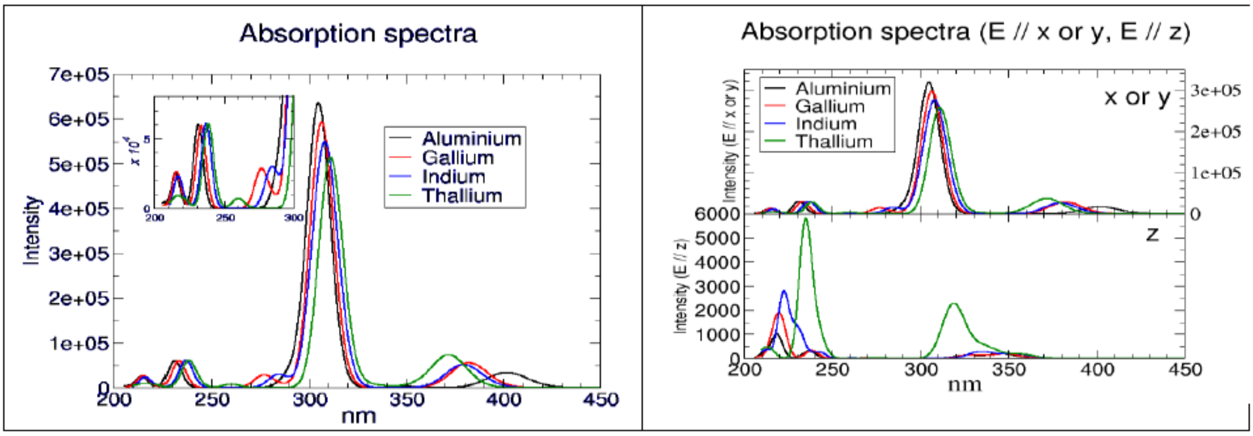

Figure 4: Absorption spectra, left total absorption intensities (inset high energy part), right top absorption intensities when the electric field is polarized in the porphyrin plane (x, y), right bottom absorption intensities when the electric field is polarized perpendicular to the porphyrin plane (z)

Compared to the experimental results, on Al and Tl in a benzene solution [11-14], these spectra are shifted towards higher energies. The solvent has certainly an important role on this point; however the TDDFT method is also known to induce systematic energy shifts on excitations. The total spectra are essentially dominated by the absorption when the electric field is oriented in the porphyrin plane (Figure 4), the absorption intensities when E//z are orders of magnitude weaker. The latter however exhibit stronger variations according to the nature of the metal. Indeed both intensities (with a strong increase from Al to Tl) and wavelengths are substantially modified. Finally, one should also point out that the electronic gap (found around 2.3 eV) does not depend much on the metal.

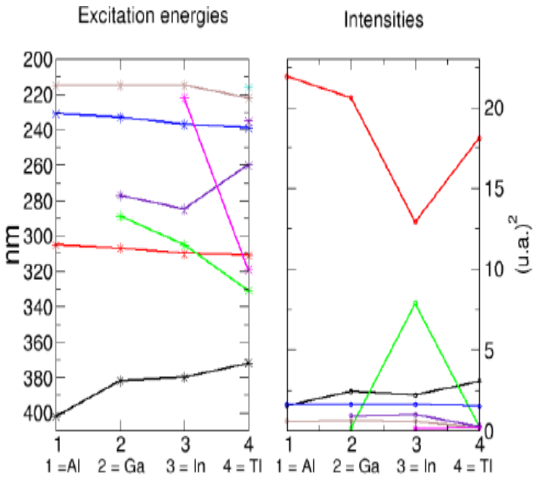

Figure 5: Excitations energies and intensities

We will now analyze the transition density matrix of the main transitions in the above spectra. Let us start with the largest peak (Figure 5). As expected, it does correspond to a quasi-degenerated double peak, associated with porphyrin π→π* excitations toward the two E_g type LUMO, LUMO+1 orbitals (Figure 6). One should note that it is a correlated excitation involving a linear combination of two quasi-particles With $\alpha^2 \simeq 0.6$ and $\beta^2 \simeq 0.3$.

$$\alpha\left[\pi(\mathrm{OEP}-\mathrm{A_{2u}}) \to \pi^*(\mathrm{OEP}-\mathrm{E_{g\,y/x}})\right] \quad + \quad \beta\left[\pi(\mathrm{OEP}-\mathrm{A_{1u}} \to \pi^*(\mathrm{OEP}-\mathrm{E_{g\,x/y}})\right] \quad + \quad \cdots$$

Unlike what was predicted in the Goutterman model [31], the hole natural orbital is not the HOMO-1 orbital involving a strong metal contribution, but a linear combination of the HOMO-1 and HOMO-2 (resp. HOMO and HOMO-3 for In and Tl) that cancels out the component on the MCH_3. Due to the lack of metal participation, its energy is only weakly shifted, towards higher wavelength as one goes down the periodic table (Figure 4 and red curve on Figure 5). For the Indium compound this excitation happens to be degenerated with a highly dispersive doubly-degenerated excitation coming from much higher energies for the lighter metals (where it can be seen in the foot of the main peak) and going to lower energy for the Thallium (see green curve on Figure 6). This excitation exhibits a low intensity for all metals but for indium, for which it mixes with the main π→π* one. It involves a metal to porphyrin charge transfer (Figure 7).

$$\sigma(\mathrm{OEP}-\mathrm{B_{2u}}) + d_{x^2-y^2}(\mathrm{M}) \to \pi^*(\mathrm{OEP}-\mathrm{E_{g\,x/y}})$$

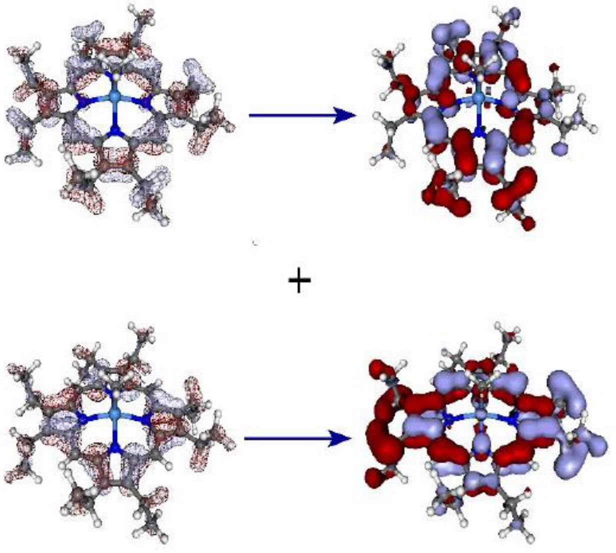

Figure 6: Transition natural orbitals for the Soret band excitation

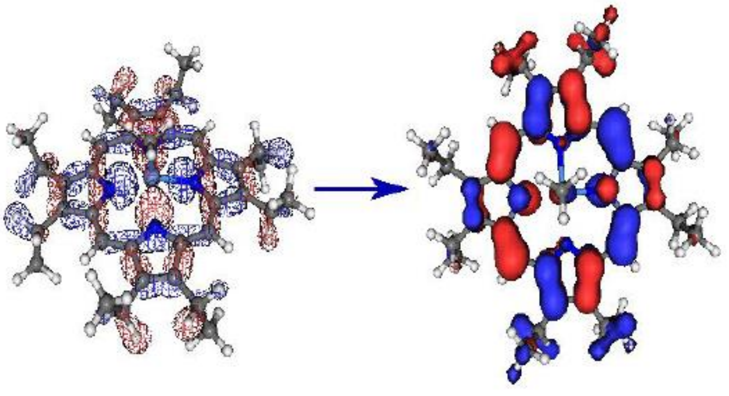

Figure 7: Transition natural orbitals for the excitation mixing with the main one for In

At lower energy there is are two more dispersive peak, hardening when the metal is going down the periodic table (Figure 4 and black curve on Figure 5). It does correspond to a doubly-degenerated excitation involving a MCH_3 to porphyrin charge transfer (Figure 8). It is again a correlated excitation involving the linear combination of two hole-particles with $\alpha^2 \simeq 80$ and $\beta^2 \simeq 20$.

$$\alpha\left[\pi(\mathrm{OEP}-\mathrm{A_{2u}}) + d_{z^2}(\mathrm{M}) + CH_3 \to \pi^*(\mathrm{OEP}-\mathrm{E_{g\,y/x}})\right] \quad + \quad \beta\left[\pi(\mathrm{OEP}-\mathrm{A_{1u}}) \to \pi^*(\mathrm{OEP}-\mathrm{E_{g\,x/y}})\right]$$

The whole natural orbital is a mixture of the HOMO-2 and HOMO-1 orbitals (for the Al and Ga), dominated by the HOMO-2. The latter however lowers in energy and becomes the HOMO-3 when going to In and Tl, resulting in the observed blue shift of the peak under consideration.

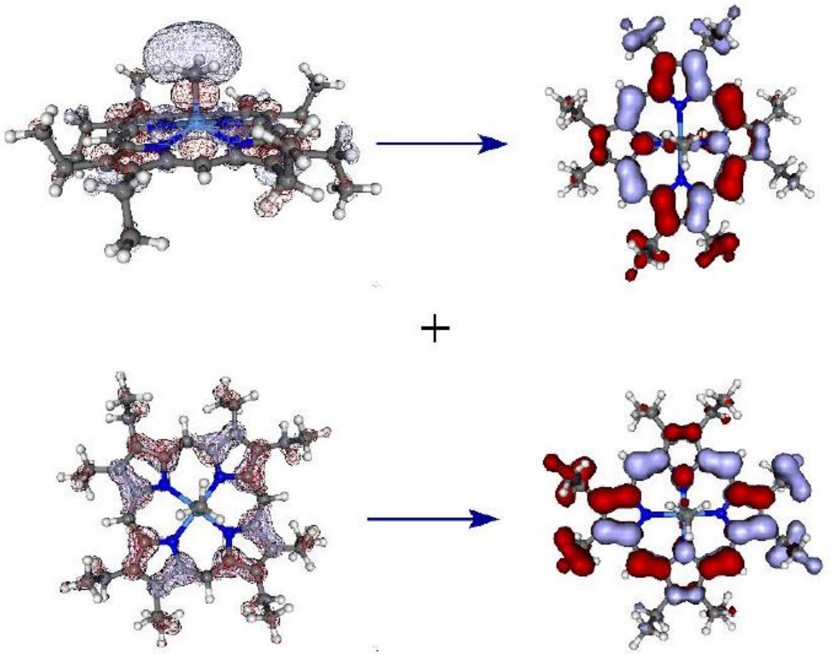

Figure 8: Natural transition orbitals of the Q band (doubly-degenerated) excitation

At this stage of the analysis one may wonder where is the HOMO→LUMO excitation, expected to be the lowest in energy. It is indeed the fact, however this excitation exhibits such a very weak intensity that it does not appear on the spectra. This is due to the OEP pseudo D_{4h} symmetry. Indeed, if the porphyrin was perfectly symmetric, this transition would be forbidden. In the present case, the small symmetry breaking associated with the presence of the MCH_3 induces a very weak intensity.

Let us now concentrate on the high energy part of the spectra. Two weakly-dispersive excitations are seen for all complexes. Again they are grouped into two sets Al/Ga and In/Tl.

$$\pi([\mathrm{OEP}-\mathrm{E_g}) \rightarrow \pi^*([\mathrm{OEP}-\mathrm{B_{1u}})$$

The lowest energy one (blue on Figure 5) corresponds to a π (OEP) $\pi \rightarrow \pi^*$ excitation with a slight component of the hole on the CH_3 (Figure 9).

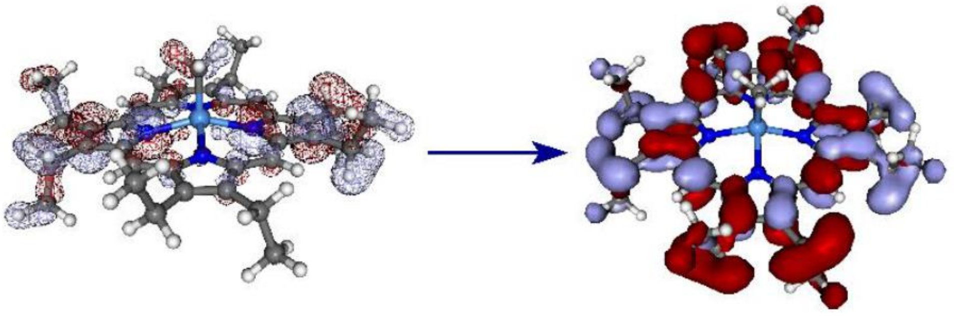

Figure 9: B1 excitation

CONCLUSION

We notice that the aluminum and gallium metalloporphyrins complexes are less stable than the indium and thallium ones. The metal of complexes is pentacoordinate and move out of the nitrogen plan around the axial ligand: out-of-plane presents two groups (Al, Ga and In, Tl). The partial charges on the nitrogen atoms are not affected by the nature of the metal for which charges differ. The metal Mulliken charges fluctuates in the same way with atoms Pauling electro negativities except for the Ga. Electronic transitions analysis of interactions between the metal and the ligand has shown that HOMO/HOMO-1 and HOMO-2/HOMO-3 have very similar energies and are exchanged between the Al/Ga and the In/Tl systems. These exchanges are related to a crossing between the energy levels of the HOMO and HOMO-1. The energy gap between LUMO and occupied orbital containing MCH_3 character decrease just a little with increasing in the atomic number of metal. This reveals a weight only on dz^2 orbital for Ga, In and Tl certainly due to the more localized nature of the Al orbital 3d. The electronic excitation spectra showed that the total spectrum is largely governed by absorption when the electric field is oriented in the plan of the porphyrin. The absorption intensities when E//z have much lower orders of magnitude but present stronger variations according to the nature of the metal.

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