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DFT and TD-DFT Studies of Mg-Substitution in Chlorophyll by Cr (II), Fe (II) and Ni (II)

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Electronic Supplementary Information (ESI) available: Cartesian coordinates and thermodynamic data for all optimized geometries and TD-DFT simulation. See DOI: 10.1039/x0xx00000x

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Abstract

Electronic contributions in electronic transitions and energetic data associated to the Mg-substitution in chlorophyll by three transition metals: chrom (Cr^{2+}), iron (Fe^{2+}) and nickel (Ni^{2+}) have been studied theoretically using Density Functional Theory (DFT) and Time Dependent Density Functional Theory (TD-DFT) methods. The binding energies are stronger than for Mg^{2+} in the case of all three cations especially in the case of Ni^{2+} . The Mg-substitution process is found to be exergonic for all title elements in gas phase and in acetonitrile using both implicit and explicit models of solvation. The natural population analysis (NPA) results, which estimated by natural bond orbital (NBO) analysis, showed significant charge transfer from pheophytin ligand to the central cation. The UV-visible proprieties of the different substitution compounds have been studied using the TD-DFT method evidencing that substitution of Mg by Cr, Fe or Ni is associated to a blue shift of the Q-band for the three cations.

Keywords:

Chlorophyll, Metal, Substitution, DFT, TD-DFT, NBO analysis.

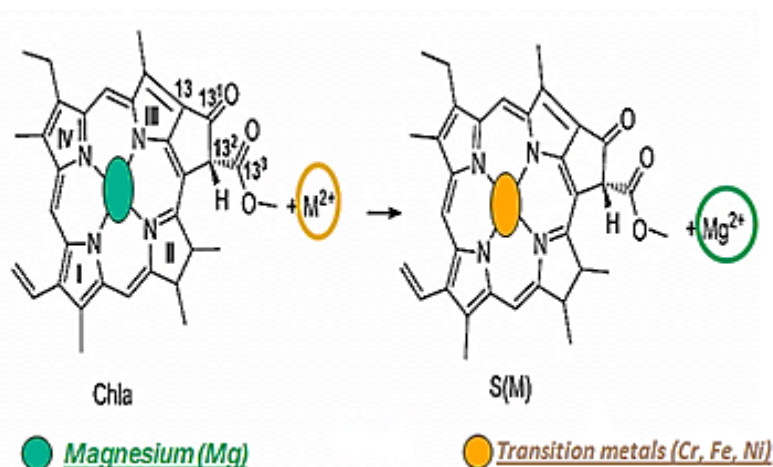
Introduction

The essential steps in photosynthesis, which is one of the most important energy-conversion mechanisms carried out for living systems, namely light harvesting (photon absorption) and charge separation, are mediated by green pigments named chlorophylls buried in the three dimensional structures of large specialized proteins fixed in cell or thylakoid membranes. Until recently, Chlorophyll (a) (Chla) was thought to be the principal photosynthetic pigment in reaction center of the photosynthetic units of all of cyanobacteria, algae and plants [1, 2]. Considerable progress has been made in the past four decades in the understanding of the in vitro properties of chlorophyll and this has contributed to a better understanding of the role of Chla at the molecular level in photosynthesis [3-6]. The salient feature of Chla relevant for its molecular organization processes is the metal bonded in the center of the tetrapyrrole macrocycle called pheophytin (Pheo). It provides the binding site to nucleophilic electron donors and it functions as a switch between various types of activities. This central pocket is occupied by the magnesium cation (Mg^{2+}) in Chla (which is thus a Pheo(Mg) complex). The association of the metal with the N-atoms from the four symmetric pyrrole rings is ensured by two covalent and two coordination bonds. In parallel, mastering the potential modulation of its properties to develop new bio-inspired tools for health [7] or energy conversion

[8] remains a major challenge to chemists [9]. In particular, the formation of bimetallic complexes proved to be an interesting direction. Plants easily absorb many toxic metals (M), most often referred to as “heavy metals” [10]. Once absorbed, they penetrate the plant tissues and in lower concentrations iron for example is an essential micronutrient for higher plants and algae and constituents of photosynthetic apparatus photosystem I and II. But higher external metal-concentrations in plants growing on soils polluted by heavy metals may produce a lot of damaging effects [11-13] among which inhibition of photosynthesis [14-16]. The exact processes remain unsure. The majority of the experiments are based on the most important site of chlorophyll (a) which is the Mg^{2+} cation bonded in the center of tetrapyrrole macrocycle called pheophytin (Pheo). Several experimental studies propose that divalent heavy metals can replace the Mg^{2+} cation of Chla to form Mg-substituted Chla complexes of general formula Pheo(M) [11, 17-21], the substitution resulting in the irreversible loss of photosynthetic activity [22, 23]. In vivo, experiments showed a spontaneous insertion of transition metals, such as Cu and Ni [11, 24, 25].

From a theoretical point of view, we have recently examined the Mg-substitution by Zn and Cu, and its competition with various chelation processes at the periphery [26]. Substitution by Cu and Zn was found to be possible and the most favored process in the case of copper when implicit solvation is included. In a second study, we examined the structural, electronic and energetic data associated to the Mg-substitution in chlorophyll (a) by three major toxic pollutants: Cd^{2+} , Hg^{2+} and Pb^{2+} . Our various approaches of free cations solvation allowed us to evidence that Mg-substitution should be possible for all title elements [27]. But the metal exchange accounting for Pheo(M) formation are still not well established for Cr, Fe and Ni. Therefore further studies are needed in order to obtain a comprehensive picture for the Mg-substitution by Cr^{2+} , Fe^{2+} and Ni^{2+} .

We thus decided to examine theoretically the structural, electronic and energetic aspects of the substitution of the Mg center of chlorophyll (a) by Cr, Fe and Ni (Scheme 1). Quantum chemical calculations at the density functional theory (DFT) have been carried out to describe the geometries of the Pheo(M) complexes. The electronic properties are then probed through NPA analysis as well as modelling of the UV-visible spectra using the TD-DFT implementation at the same computational level as geometry optimization. The results are analysed and compared with those obtained from experimental studies.



Scheme 1: Mg-Substitution process in Chlorophyll (a).

Computational details

Computations have been carried using the Gaussian 09 [28] program within the framework of the density functional theory at the B3LYP/6-31G* level [29-31], Closed-shell system, namely Mg^{2+} ($3s^03p^0$), but also Ni^{2+} ($4s^03d^84p^0$), Cr^{2+} ($4s^03d^44p^0$) and Fe^{2+} ($4s^03d^64p^0$) in their singlet states were carried out using spin restricted formalism. On the other hand, open shell systems, namely Ni^{2+} in its triplet state, Cr^{2+} and Fe^{2+} in theirs triplet and quintuplet states have been studied using a spin-unrestricted formalism. The lowest energy spin states calculated are the one retained for the following discussion. They were found to be the triplet state for Ni^{2+} ion (both naked and coordinated to six molecules of acetonitrile) and the singlet for the complex formed with chlorophyll (a) (Pheo(Ni)). For Fe, the more stable spin states were calculated to be the quintuplet state for Fe^{2+} ion (both naked and coordinated to six molecules of acetonitrile) and the triplet for the complex formed with chlorophyll (a). The studied Cr^{2+} derivatives are always more stable in its quintuplet state. These results are in line with electronic structures obtained for porphyrin complexes [32]. They are all consistent with a simple molecular orbitals model based on the 3d orbital splitting [33]. The solvated structures are in a low-field (small Δ value, see Fig.1) high- spin octahedral like arrangement. The Pheo(M) complex corresponds to a high- field (large Δ) low-spin square planar electronic arrangement (Fig.1).

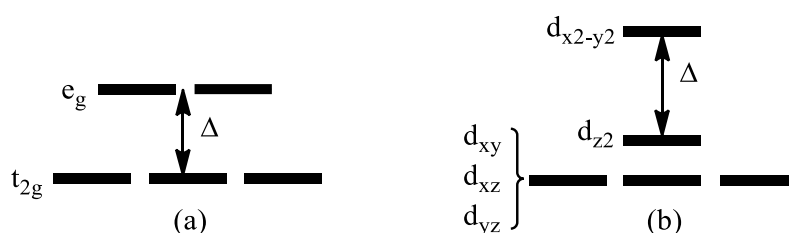


Fig. 1. Model 3d orbital splitting: a) octahedral-like ; b) square-planar like. Adapted from ref. 32

Calculations were based on a Chla model containing 73 atoms reported in Scheme 1 which was proposed in our previous work [26, 27, 34]. This model retains the structure of Chla except for the phytol ester side chain which was replaced by a methyl group to reduce the number of atoms for computation.

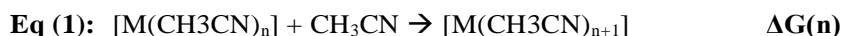
The geometries were fully optimized in the gas phase and vibrational frequencies were computed in the harmonic approximation to confirm structural assignment to energy minima and contributions to Gibbs free energies. Empirical corrections for dispersion were evaluated through single point calculations using DFT-D3(BJ) corrections [35].

Chla and its substitution complex (Pheo(M)) can accommodate additional solvent molecules on the central cation, in addition to the tetracoordination of the Pheo ligand through binding of acetonitrile which was used as a model solvent in our previous works about the interaction of different heavy metals with chlorophyll (a) [26, 27]. This solvent has been chosen as it cannot form H-bonds with the C=O groups of chlorophyll (which would be artefact toward the examined properties) and has been recently used as solvent for a detailed experimental study of transmetallation of substituted chlorophylls [36].

The Gibbs free binding energy of the first acetonitrile ligand, including all thermal corrections; BSSE, dispersion corrections and ZPE computed in the harmonic approximation, varies from slightly exothermic for Mg^{2+} ($-2.4 \text{ kcal mol}^{-1}$) to slightly endothermic for Ni^{2+} and Cr^{2+} ($+5.0$ and $+3.3 \text{ kcal mol}^{-1}$ respectively).

As such, Chla should be considered as monosolvated, whereas Pheo(Ni) and Pheo(Cr) should be considered as non-solvated. Nevertheless, this difference in solvation does not yield significant variations in the substitution free energies (only a 2.4 kcal mol⁻¹ difference). As a consequence, for the sake of homogeneity, no solvation will of Pheo(M), whatever the nature of M.

We followed the same calculation strategy to model the free cations, we examined the explicit coordination of the different cations M²⁺ with acetonitrile (MeCN) molecules (Eq. 1) to result in [M(MeCN)_n]²⁺ complexes. For each metal (Mg, Cr, Fe and Ni), the number of acetonitrile molecules ‘n’ to be added was chosen as the smallest ‘n’ value for which the Gibbs free energy ΔG(n) for equation 1 is positive.



The results for the isolated cations Mg²⁺, Cr²⁺, Fe²⁺ and Ni²⁺ are gathered in Table 1. Gibbs free energies for coordination of an additional solvent molecule to [M(MeCN)₆]²⁺ complex, including all thermal corrections (BSSE, dispersion and ZPE), is strongly positive (> 10 kcal mol⁻¹) in the case of Mg, slightly negative in the case of Cr and Ni (-1.3 kcal mol⁻¹ and -1.7 kcal mol⁻¹ respectively) and optimization is even impossible in the case of iron (Fe) as decoordination of the MeCN molecule occurs during the course of the optimization. As a consequence, and for the sake of homogeneity, six-solvated cations will be used to model the structure of all free cations in acetonitrile.

Table 1 Gibbs Free energies (ΔG(n) in kcal mol⁻¹) ΔH(n) in kcal mol⁻¹ is given in parenthesis) for the coordination of an additional acetonitrile molecule to the [M(MeCN)_n]²⁺ complex

	Mg ²⁺	Cr ²⁺	Fe ²⁺	Ni ²⁺
n = 3	-39.9 (-49.1)	-48.3 (-53.1)	-37.4 (-48.8)	-44.8 (-55.9)
n = 4	-19.2 (-27.2)	-17.3 (-28.9)	-15.9 (-23.9)	-19.8 (-31.2)
n = 5	-11.4 (-26.4)	-7.6 (-16.7)	-6.4 (-23.6)	-15.6 (-24.3)
n = 6	10.6 (-0.7)	-1.3 (-12.1)	Not obtained	-1.7 (-12.4)

Modelling of the UV-Vis spectra was carried out using the TD-DFT implementation [28] at the B3LYP, CAM-B3LYP and BP86 functionals in the gas phase and at B3LYP functional with implicit solvation in acetonitrile (see Sup. Info). NPA population analyses were carried out using the NBO version [37] implemented in Gaussian.

Results and Discussion

Structural properties

In the first part, we analyzed the structural properties of the optimized geometries in the gas phase for the complexes formed by substitution of the central Mg atom by Cr, Fe and Ni. Before considering the stability

of Pheo(M) complexes, some general comments can be made on their structures. The main results of the geometry optimization of the Pheo(M) monomer are reported in Table 2. At first glance, it can be seen that the metal cation, native (Mg) or substituted (Cr, Fe or Ni), is located at the center and in the plane of the chlorin ring. The value obtained for Mg is in good accord with experimental X-ray results for chlorophylls and bacteriochlorophylls in protein [38-40].

The substitution retains the order of M-N bond distances of Chla which is reported experimentally [38, 39] and theoretically [41, 42] but the average $\langle M-N \rangle$ and the out-of plane distortions vary with the metal.

Table 2 Geometric (distances in Å) and E_{bind} (in kcal mol⁻¹) parameters for Pheo(M) complexes.

	Mg ²⁺	Cr ²⁺	Fe ²⁺	Ni ²⁺
Spin multiplicity	1	5	3	1
$\langle M-NNN \rangle^{[a]}$	0.004	0.004	0.005	0.009
M-N(I) ^[b]	2.031	2.027	2.015	1.979
M-N(II) ^[c]	2.149	2.109	2.152	2.121
M-N(III) ^[d]	2.017	2.003	2.007	1.962
M-N(IV) ^[e]	2.074	2.041	2.066	2.028
$\langle M-N \rangle^{[f]}$	2.068	2.045	2.060	2.022
$\Delta(M-N)^{[g]}$	0.132	0.106	0.145	0.159
$E_{\text{bind}}^{[h]}$	-721.6	-762.6	-758.8	-815.6

[a] $\langle M-NNN \rangle$ is out of the plane distortions.

[b, c, d, e] M-N bond distances between the central metal and the four nitrogen atoms (Scheme 1).

[f] The average of the M-N distances.

[g] $\Delta(M-N)$ is the difference between the longer and the shorter M-N bond.

[h] $E_{\text{bind}} = E(\text{Pheo}(M)) - (E(M^{2+}) + E(\text{Pheo}))$.

Correlation between the geometric and energetic data for binding within Pheo(M) can be gleaned from the binding energies in Table 2.

The binding energies (E_{bind}) were first computed as the interaction between two charged fragments, the dianionic Pheo ligand and the dicationic metal ion according to Eq (2).

$$\text{Eq (2) : } \quad E_{\text{bind}} = E(\text{Pheo}(M)) - (E(M^{2+}) + E(\text{Pheo}))$$

The calculated binding energies of the substitution metals are all more negative than for the native one and are quite sensitive to the nature of the metal (as a 100 kcal.mol⁻¹ variation is observed, despite the similarity of the charges of the metal cations). They vary in the order: Mg > Fe > Cr > Ni. The trend in the binding energies parallels the $\langle M-N \rangle$ bond length in that large absolute values of E_{bind} are associated with shorter M-N bond distances.

Electronic properties

The population analysis of the Chla model and of the three substitution compounds Pheo(Cr), Pheo(Fe) and Pheo(Ni) reveals that the charge on the central atom is smaller in the Pheo(Fe) and Pheo(Ni) compounds, compared to chlorophyll, but it is bigger in the case of Cr (1.437 vs 1.413 for chlorophyll (a)). Even though the central atom

formally bears in all cases a +2 charge, all the cations have a computed charge significantly smaller to +2, as expected from the strong charge transfer from the Pheo macrocycle to the central cation. The charge transfer nevertheless remains significantly smaller than 1 e. A population analysis of the valence shell allows decomposing this charge transfer. In the singlet state of Pheo(Ni) the charge transfer (0.783 e) is distributed essentially on orbital 4s (0.43) with a smaller overpopulation of the d shell (8.33 instead of 8). The population analysis of the valence shell of Pheo(Cr) showed the charge transfer is equal to 0.563 e and decomposes on the 4s orbitals (0.33 e) and in a smaller extent on an overpopulation of the d shell (4.21 instead of 4 e). A similar result is obtained for Fe: 0.46e on the 4s orbitals, and overpopulation by 0.27 e on the 3d orbitals.

Table 3 NPA charge, population and Q_y state (transition wave length in nm, oscillator strength in parenthesis) of Pheo(M) complexes in their stable states

	Mg ²⁺	Cr ²⁺	Fe ²⁺	Ni ²⁺
NPA charge	1.413	1.437	1.343	1.218
Valence pop NPA	3s(0.26) 3p(0.32)	4s (0.33) 3d (4.21) 4p (0.02)	4s (0.37) 3d (6.27) 4p (0.02) 5s (0.01)	4s (0.43) 3d (8.33) 5s (0.01) 5p (0.02)
Q _y state (B3LYP (gas))	579.6 (0.24)	564.9 (0.14)	573.6 (0.13)	576.6 (0.25)

We next tried to evaluate the UV-visible properties of these substitution compounds (Table 3). The Q-band of chlorophyll can be quite easily reproduced computationally as it is made of a single strong transition at 579.6 nm (Q_y, whereas Q_x participation to the band maximum remains negligible). As this is not the case for the B-band (B₁ transition at 391.6 nm and B₂ at 373.1 nm, see Sup. Info.), and in line with our previous studies [26, 27], we focused only on the Q_y transition. A blue shift is observed when going from Mg to metals of line 4. This shift decreases when going from Cr to Ni (14.6 nm, 6.6 nm and 3 nm for Cr, Fe and Ni respectively). We concluded so, that substitution of Mg by Cr, Fe or Ni is associated to a small blue shift of the Q-transition for the three cations. Let us also mention that the oscillator strength is two time smaller in the case of Cr and Fe (open shell systems).

Better understanding of the nature of this shift can be found in a frontier molecular orbitals (FMOs) analysis [43-46]. The TD-DFT calculations reveal the main molecular orbitals contributing in the Q_y electronic transition, which will be discussed in the following. The Q_y transition of Chla is attributed to electronic excitations from HOMO to LUMO (85%) and from HOMO-1 to LUMO+1 (14%) (Fig. 2).

This result is in a good agreement with the observed UV-Vis absorption spectra of Chla that obtained theoretically using TD-DFT method [47-49].

A very similar result seems to be obtained for Pheo(Ni) as the Q_y transition at 576.6 nm (f=0.246) in the UV-Vis spectrum is found to be associated to two electronic excitations, from HOMO to LUMO (89%) and from HOMO-1 to LUMO+1 (8%) (Fig. 3).

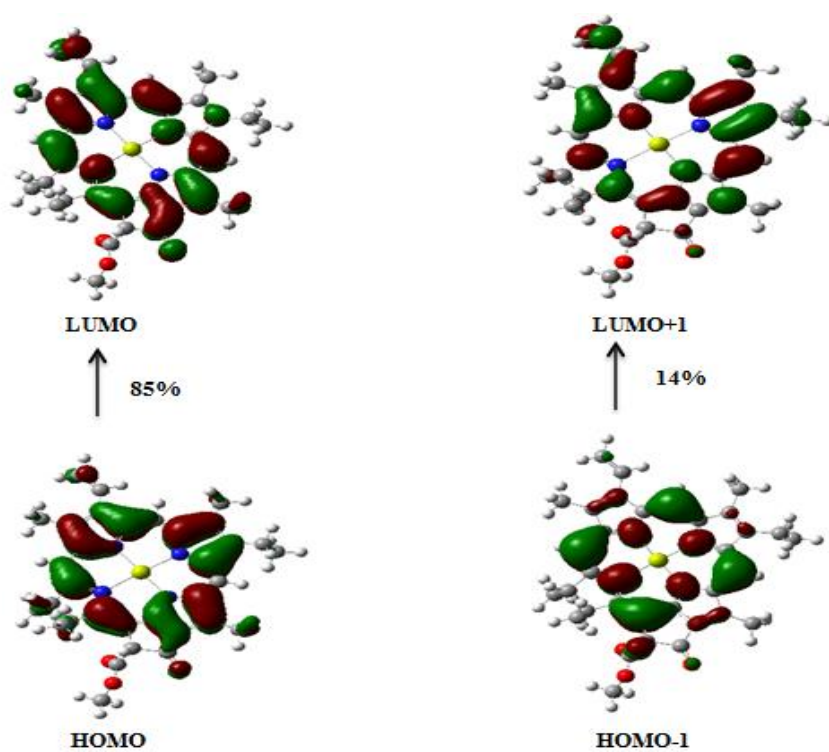


Fig. 2 Frontier molecular orbitals and associated electronic transitions of Qy band (579.6 nm) for (Chla) calculated at B3LYP/6-31G* level.

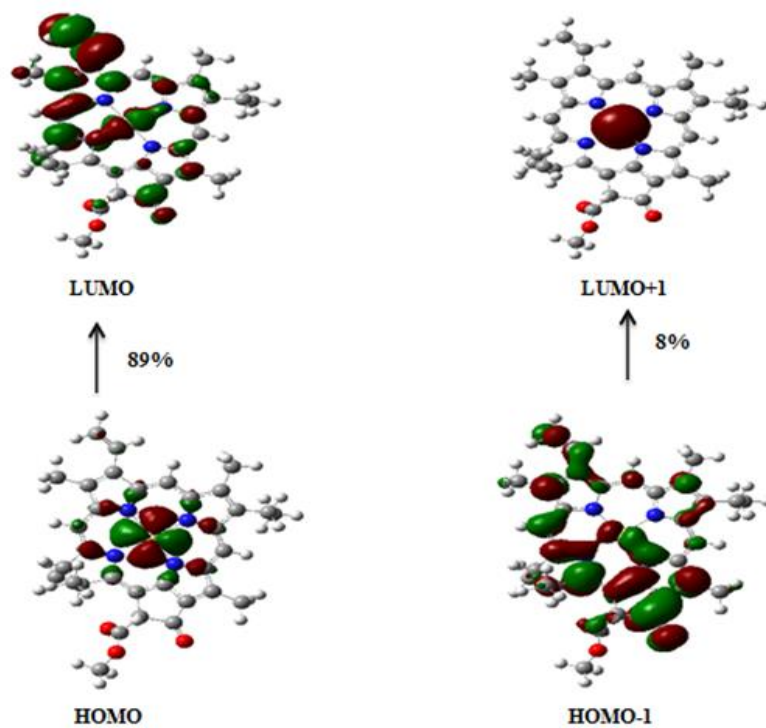


Fig. 3 Frontier molecular orbitals and associated electronic transitions of Qy band (576.6 nm) for (Pheo(Ni)) calculated at B3LYP/6-31G* level.

Nevertheless, a close examination of different molecular orbitals presented in Fig. 2 and Fig. 3, we found a very different spatial distribution of electron. Indeed, whereas in the case of Chla, all four orbitals involved are distributed on the porphyrin ring, HOMO and LUMO+1 are metal centered in the case of Pheo(Ni), so that the transition in the latest complex is mainly (89%) metal \rightarrow ligand electron transfer, and more weakly (8%) ligand \rightarrow metal.

The results are more complex to decipher in the case of Cr and Fe as, since they are open shell systems and don't exhibit a strongly dominating contribution to the Q_y band. As a consequence, only contribution larger than 10% will be discussed. For Cr, the Q_y transition is located at 564.9 nm with oscillator strength of 0.1385 and attributed mainly to (Figure 4); HOMO-3(α) \rightarrow LUMO(α) (34%), HOMO-2(α) \rightarrow LUMO(α) (19%), HOMO-1(α) \rightarrow LUMO(α) (26%), HOMO(α) \rightarrow LUMO(α) (52%) and HOMO(β) \rightarrow LUMO(β) (32%). As evidenced, all contributions end up in the LUMO (either α or β). When looking into more details in the spatial distribution of the orbital, they are essentially ligand centred, so that all transition can be seen as intra-ligand excitations (Fig. 4). Nevertheless, in contrast with Chla, a small metal contribution is observed on most orbitals.

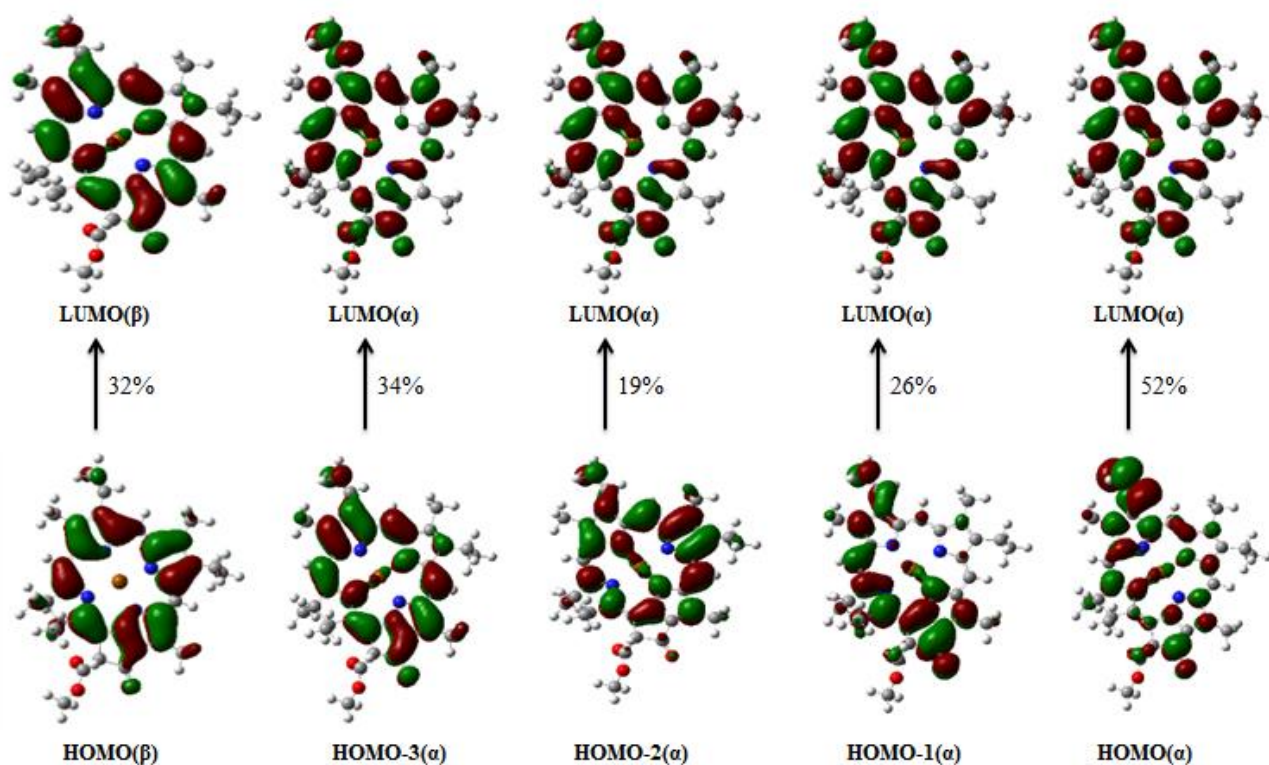


Fig. 4 Molecular orbitals and associated electronic transitions of Q_y band (564.9 nm) for (Pheo)(Cr) calculated at B3LYP/6-31G* level.

A similar observation can be made in the case of Pheo(Fe). We found only one alpha electronic excitation from HOMO to LUMO (61%) attributed to the Q_y transition at 573.7 nm with an oscillator strength 0.1266 and several β transitions: HOMO-2(β) \rightarrow LUMO+1(β) (30%), HOMO-1(β) \rightarrow LUMO(β) (65%), HOMO(β) \rightarrow LUMO+1(β) (19%). As for Cr, most transition are between ligand centered orbitals, with a minor contribution of the metal center (Figure 5). The latter nevertheless seems most important than for Cr.

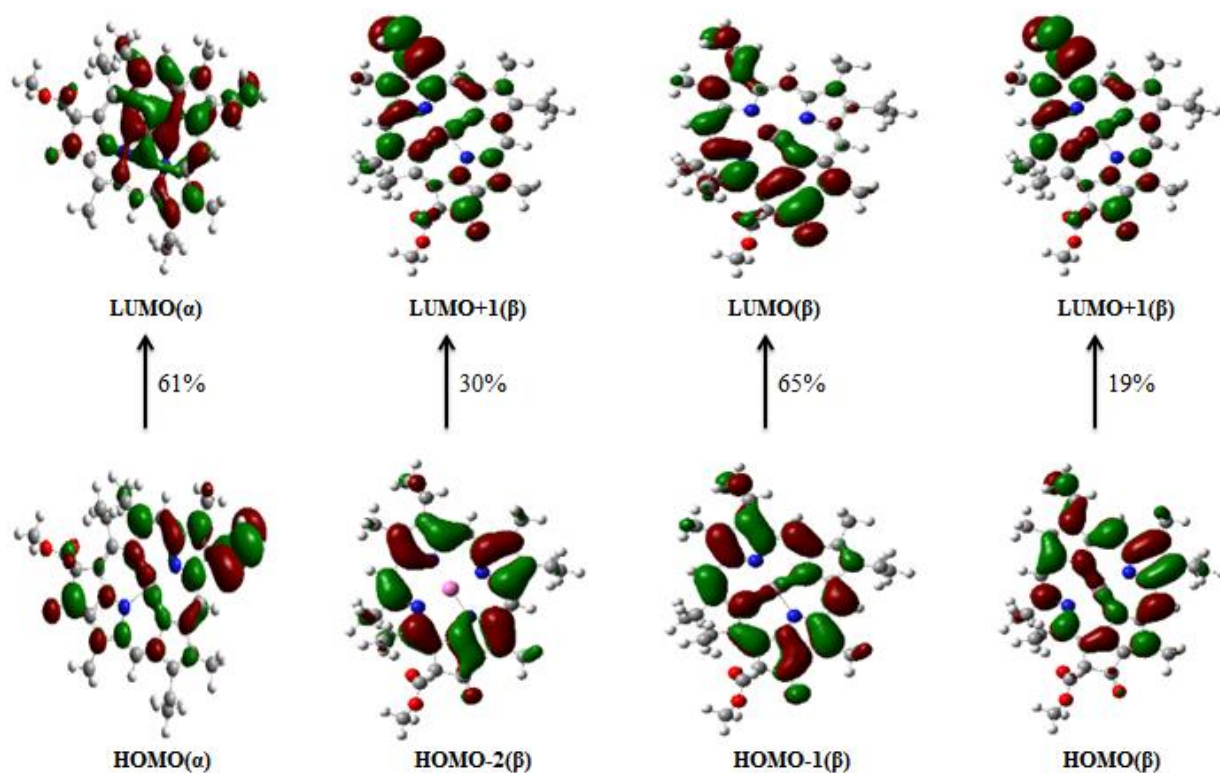


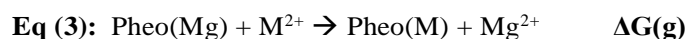
Fig. 5 Alpha and Beta Frontier molecular orbitals and associated electronic transitions of Qy band (573.7 nm) for Pheo(Fe) calculated at B3LYP/6-31G* level.

As a conclusion, in most of the observed transition, the structure of the porphyrin ring is responsible for electronic transitions in Pheo(M) complexes. This result is in agreement with previous theoretical study of chlorophyll [47] and metalloporphyrin [50]. Charge transfers between metal and ligands are only observed in the case of Ni, despite the apparent similarity of the UV-visible spectrum.

Energetic properties

The thermodynamic data of the Pheo(M) coordination, cation binding and exchange (Mg-substitution) process are examined in this part.

Let us first comment the results of Mg-substitution in gas phase (Eq 3) which can be directly connected to the binding energy reported above.



The Gibbs free energy of the substitution process (Eq (3)) $\Delta G(\text{g})$ is reported in Table 4. The substitution process is found to be strongly exothermic ($\Delta H < 0$) and exergonic ($\Delta G < 0$). The extent of the stability follows the order: $\text{Ni}^{2+} > \text{Cr}^{2+} > \text{Fe}^{2+}$. However, these results cannot be used to predict the thermodynamic of the reaction in solution as it requires taking into account solvent binding, not only in chlorophyll and in its substitution complexes, but also when the cation is free in solution.

Table 4 Energetic data (in kcal mol⁻¹) for Pheo(M) complexes

	Mg ²⁺	Cr ²⁺	Fe ²⁺	Ni ²⁺
$\Delta G_{(g)}^{[i]}$	-	-40.3	-37.0	-92.4
$\Delta E_{MeCN}^{[j]}$	-20.4	-8.0	-3.8	-6.2
$\Delta G_{MeCN}^{[k]}$	-7.9	3.6	7.8	3.9
$\Delta G_s (M^{2+})^{[l]}$	-323.9	-338.1	-339.3	-395.6
$\Delta G_{explicit}^{[m]}$	-	-26.2	-21.8	-20.8
$\Delta G_{explicit/implicit}^{[n]}$	-	-23.3	-12.3	-14.7

[i] The Gibbs free energy of the substitution process in gas phase.

[j] Binding energy of Pheo(M) complexes with one acetonitrile molecule including BSSE and dispersion corrections.

[k] The Gibbs free energy of Pheo(M) complexes with one acetonitrile molecule including all thermal corrections (BSSE, dispersion corrections and ZPE).

[l] The Gibbs free energy of the free cation coordination with six acetonitrile molecules.

[m] The Gibbs free energy of the substitution process using explicitly solvated cations.

[n] The Gibbs free energy of the substitution process using a mixed explicit/implicit solvation model

Evaluation of the substitution process is obtained by computing the Gibbs free energy using explicitly solvated cations $\Delta G_{explicit}$ (Eq 4, Table 4):



Mg-substitution is still favored with Cr²⁺, Fe²⁺ and Ni²⁺, but it appears that the explicit solvation model in the case of acetonitrile reduces significantly the exergonicity of exchange, which can be associated with the fact that acetonitrile coordinates less strongly with Mg²⁺ (-323.9 kcal mol⁻¹; coordination Gibbs free energies of six acetonitrile molecules) than the other metals (-395.6 kcal mol⁻¹ for Ni²⁺, -339.3 kcal mol⁻¹ for Fe²⁺ and -338.1 kcal mol⁻¹ for Cr²⁺). This is similar to the experimental hydration free enthalpies [51] of Fe²⁺ (-440.2 kcal mol⁻¹), Cr²⁺ (-442.6 kcal mol⁻¹) and Ni²⁺ (-473.7 kcal mol⁻¹) which are stronger than Mg²⁺ (-437.8 kcal mol⁻¹). Therefore, desolvation of the metal cation which is necessary for the substitution, strongly disfavors the substitution. Gibbs free energies using the explicit model of solvation ($\Delta G_{explicit}$) were found following the order Cr > Fe > Ni.

Finally, we decided to probe another correction to the explicit model commonly proposed in the literature. Continuum solvation effects were incorporated, leading to $\Delta G_{explicit/implicit}$ computed according to a mixed explicit/implicit solvation model [52].

Correction using single point PCM calculations does not modify the exergonicity of exchange, but it results an inversion in the order of the thermodynamic stabilities ($\Delta G_{explicit/implicit}$): Cr > Ni > Fe. This calculations lead to an important correction in all cases by increasing the Gibbs free energies; by 2.9 kcal mol⁻¹, 6.1 kcal mol⁻¹ and 9.5 kcal mol⁻¹ for Cr, Ni and Fe respectively which indicates that implicit solvation opposes the substitution with these three metals. We examined the origin of this effect. Surprisingly, the principal corrections of Gibbs free energies using the implicit solvation were associated with the effects in the $[M(\text{MeCN})_n]^{2+}$ complexes (correction about -135.8 kcal mol⁻¹ in the case of Mg²⁺, -120.0 kcal mol⁻¹ for Ni²⁺, -118.9 kcal mol⁻¹ for Fe²⁺ et -118.8 kcal mol⁻¹ for Cr²⁺).

Conclusions

We have studied the substitution of the central cation Mg^{2+} of chlorophyll (a) by three dicationic transition metals, Cr^{2+} , Fe^{2+} and Ni^{2+} . The substitution is found to be energetically favored and leads to compounds with very similar electronic and geometric properties of those of chlorophyll (a). The substituted complex does not permit the coordination of the apical ligand to the central metal and the different models of solvation, explicit or explicit/implicit, opposes the substitution in the case of acetonitrile and reduces significantly the exergonicity of exchange but it is still favored in all title elements.

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