

Semi-empirical Investigation of Geometrical and Electronic
Properties of Transition Metal-Phthalocyanines (metal=Co,Ni,Cu)
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Abstract

Three transition metal-Phthalocyanines are investigated (metals= Co,Ni,Cu) using semi-empirical methods. PM3 and ZINDO/S have been used because they maintain transition metal parameters. PM3 has been used for geometrical optimizations, while ZINDO/S has been used for single point calculations to predict the electronic energy states. The last one is showed better results for single point calculations while the former was better for geometrical optimizations. The symmetries reached were D_{4h} for CuPc while it was D_{2h} for CoPc and NiPc. The obtained bond lengths compared with reported experimental and more sophisticated theoretical methods values. The results were in good agreement. The obtained molecular orbital energies were of reasonable accuracies. Nevertheless, these methods are much faster when compared with expensive Ab-initio methods that need high performance expensive computers. Three dimensional plotting of electronic charge distributions and electrostatic potential isosurfaces have been plotted as well.

دراسة شبة تجريبية للخواص الهندسية والالكترونية (المعدن = Cu, Ni, Co)

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الخلاصة

أجريت حسابات شبة عملية على ثلاث جزيئات (فتالوسيانين-المعادن الانتقالية) باستخدام طريقتين (PM3) و (ZINDO/S) اللتان توفران معاملات العناصر الانتقالية. استخدم (PM3) لحسابات ضبط الشكل الهندسي وتمت مقارنة أطوال الأواصر مع القيم المسجلة والعملية والنظرية بطرق أكثر تعقيداً وكلفة.

النتائج كانت مقارنة بشكل جيد للنتائج المنشورة. أما الحسابات لمستويات الطاقة الجزيئية فقد استخدم (ZINDO/S) لأنه لأظهر دقة أحسن من (PM3). وكانت النتائج مقبولة مقارنة بالنتائج المحسوبة بطريقة (DF).

أظهر البحث أنه يمكن الاعتماد على طريقة (PM3) لحسابات ضبط الشكل الهندسي ولكنها ذات اعتمادية أقل فيما يتعلق بحسابات مستويات الطاقة. إلا أن هذه الطرق أسرع بكثير وأقل كلفة من مثيلاتها التي تعتمد الطرق المعقدة والتي تحتاج إلى حاسبات ذات كفاءته عالية. وتم رسم أشكال بعض الأوربيتالات العلوية المهمة بالإضافة إلى التوزيع الإلكتروني للجزيئات وثلاث أبعاد أيضاً.

Introduction

Phthalocyanines (Pc's) and metallophthalocyanines (MPc's) are important class of molecular functional materials that show interesting physical and chemical properties. These macrocyclic molecules are of great diversity of technological applications^[1].

Pc's outstand within the fields of materials science and nanotechnology, because to their electrical properties, their strong absorption in the visible region, their thermal and chemical stability and capability of supporting intense electromagnetic radiations. Another remarkable feature is their versatility; the two hydrogen atoms of the central cavity can be replaced by more than 70 metals and a variety of substituents can be incorporated, both at the periphery of the macrocycle and/or at the axial positions, thus allowing fine tuning of the physical properties^[2]. Because of the versatile chemistry of Pcs, their assembly into multicomponent photo and electroactive systems can be easily performed through the linkage with appropriate units, which broadens the applicability of this type of macrocycles, for example in the processing of light into chemical or electrical energy^[2].

To date phthalocyanines have been shown to complex alkali metals, alkaline earths, metals and metalloids of the p-block, and majority of the transition metals, silver and mercury are the only transition metals not to form complexes with them.^[3]

Pc's are planar aromatic macrocycles consisting of four isoindole units presenting an 18 pi-electron aromatic cloud delocalized over an arrangement of alternated carbon and nitrogen atoms. For many years, Pcs have been an important article of trade, i.e., dyestuffs for textiles and inks, as a consequence of their dark green-blue color: their absorption spectra show, in fact, an intense Q-band in the visible region, usually centered at 620–700nm^[4]. Spectral properties of phthalocyanines are central to their chemical and electronic properties. The spectra of Pcs are governed by 18 system of the inner 16-membered ring.

Although the special nature of phthalocyanines and their metal complexes has been known for decades, their uses as commercial dyes, catalysts, optical and electrical materials are expanding enormously every year. Pcs are used as sensors in conducting polymers, batteries^[5] and liquid crystals^[6]. Unsubstituted and substituted Pcs are widely used as agents in the photodynamic therapy (PDT) of cancer^[5,7]. Phthalocyanines find their usefulness in emerging technologies such as catalysis, nonlinear optics, gas sensors, thermal writing displays, and solar cells^[8,9].

Moreover, there are ideas to develop low dimensional molecular magnets and organic based spintronics. The molecular magnets are assumed as possible candidates for potential applications in high-density information storage and quantum computers, while molecular spintronics devices have attracted enormous attention because they are supposed to be faster and to consume less power. In FETs based on these materials, it may be possible to induce and control electrostatically the magnetic properties of organic materials, just by tuning the density of mobile charge carrier that mediate interactions between the local spins^[10,11]. More recently, Pcs have emerged as attractive molecular building blocks for their arrangement into molecular materials and nanotechnological devices^[12].

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The successful incorporation of Pcs into devices requires a fine control of the spatial arrangement of these macrocycles with respect to each other, as an appropriate supramolecular organization of the chromophores allows the expression of their optoelectronic properties to a maximum level. Specificity in the applications of phthalocyanines can be introduced by modification of the phthalocyaninering, by changes in the central metal as in the present work or axial ligands.

Metal-phthalocyanines (MPC's), are a large class of materials with isostructural molecules that differ by only one atom (the metal element). This metal atom determines the electronic properties of the molecules, including the spin S in the molecular ground state [13, 14].

The large size and complexity of MPC's ($C_{32}H_{18}N_8M$) makes it difficult to use standard ab initio methods [15,16] especially we are using a PC computer to perform calculations. Fortunately, the PM3 semi-empirical method can handle organometallic molecules much faster compared to time consuming ab initio methods and capable to manage transition metal atoms.

The aim of this work is to investigate the effect of replacing the two central hydrogen atoms by three transition metals Cu, Co (open $(n-1)d$ shells), Ni(closed shell) on both structural and electronic properties. Nowadays, CoPc is considered as a material for development of low dimensional molecular magnets [17].

In this work, the computations made use the PM3 and ZINDO/S semi-empirical methods that are implemented within the software Hyperchem-8 [18].to geometrically optimize three transition metal MPC's (M=Cu, Ni, Co) which extend over $3d^9-3d^8$ complexes. Single point calculations were performed to get their electronic structures, orbitals, total charge densities and electronic potential.

Computational methods & details:

Computational methods can provide a reasonable basis for the interpretation of experimental data and shed light on the underlying physics and chemistry of such systems. Also, they generate data which complements experimental data on the structure, properties and reaction of substances. These methods rely on models originated from classical and quantum physics to explain and interpret the behavior of atoms, molecules, clusters and solids.

There are three main types of calculations [19,20].

- i) Ab initio methods: (Latin expression means 'from scratch') in these methods molecular structures can be calculated using only: Schrödinger equation, the values of the fundamental constants and atomic numbers of the present atoms.
- ii) Semi-empirical methods: are techniques originally approximations of Ab initio methods which use approximations from empirical (experimental) data to provide the input into the mathematical models.
- iii) Molecular mechanics: These methods use classical physics to predict the behavior of molecules.

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Computational methods are particularly useful for determining molecular properties, which are inaccessible experimentally and for interpreting experimental data. With computational methods, one can perform: electronic structure determinations, geometry optimization, frequency calculations, transition structures location, electron and charge distributions analysis, potential energy surfaces (PES), kinetic, and thermodynamic calculations.

Molecular mechanics methods(although they are fast and very efficient when dealing with large molecules)are generally unable to treat metals. This is because metals have a wide range of valences, oxidation states, spin multiplicities, and have unusual bonding situations (e.g., $d\pi-p\pi$ back bonding). In addition, the non-directional nature of metallic bonding is less amenable to a ball and spring interpretation.

At the present work, all calculations were performed using the *Parametric Method3*(PM3) model, developed by James Stewart, uses a Hamiltonian that is very similar to the AM1 (Austin Model 1) Hamiltonian, but the parameterization strategy is different. semi-empirical methods were used for time consuming geometry optimization. Semi-empirical methods are computationally fast because many of the difficult integrals are neglected and they compensated through the use of parameters.Nevertheless, these methods produced a good accuracy within a reasonable computing time.Semi-empirical methods continue to be developed because there is always room for improvement of the parameterization scheme and the use of experimental data.

PM3method uses a minimal basis set of valence Slater type s and p atomic orbitals (AO)s to expand valence-electron molecular orbitals(MO)s^[19].

This method is re-parameterization of the MNDO method and in general has been found to give better bond lengths, ionization energies, and enthalpies of formation than the MNDO schemes.

In MNDO method, compounds containing H, Li, Be, B, C, N, O, F, Al, Si, Ge, Sn, Pb, P, S, Cl, Br, I, Z n, and Hg have been parameterized. The MNDO Fock matrix elements can be determined as follows:^[20]Core matrix elements (core resonance integral)

$$H_{\mu_A \nu_B}^{Core} = \langle \mu_A(1) | \hat{H}^{Core}(1) | \mu_A(1) \rangle$$

with atomic orbitals centered at atoms A and B are given by:

$$H_{\mu_A \nu_B}^{Core} = \frac{1}{2} (\beta_{\mu_A} + \beta_{\nu_B}) S_{\mu_A \nu_B}; A \neq B$$

where β are the parameters for each orbital. Core matrix elements from different atomic orbitals centered on the same atom are given by:

$$H_{\mu_A \nu_B}^{Core} = \left\langle \mu_A \left| -\frac{1}{2} \nabla_1^2 + V_A \right| \nu_A \right\rangle + \sum_{B \neq A} \langle \mu_A | V_B | \nu_A \rangle$$

Using group theoretical considerations can be made as zero. Hence:

$$\langle \mu_A | -\frac{1}{2} \nabla_1^2 + V_A | \nu_A \rangle$$

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$$H_{\mu_A \nu_B}^{\text{Core}} = \sum_{B \neq A} \langle \mu_A | V_B | \nu_A \rangle$$

In PM3, compounds containing H, C,Si, Ge,Sn,Pb,N,P, As,Sb,Bi, O,S, Se,Te,F, Cl, Br,I,Al,Ga,In,Tl,Be, Mg,Zn,Cd, and Hg have been parameterized^[18,20].

The three semi-empirical methods MNDO, AM1,and PM3 do not use d-orbitals in their basis sets.We are about to examine how far this method is reliable to produce the electronic geometrical and electronic structure of three transition metal-phthalocyanine of different electronic configurations.

ZINDO/S is parameterized to reproduce spectroscopic transitions, therefore it is not recommended using this method for geometry optimization. However, better results may be obtained by performing a single-point calculation with ZINDO/S on a geometry obtained from an optimization using one of HyperChem's other methods, or an external source.

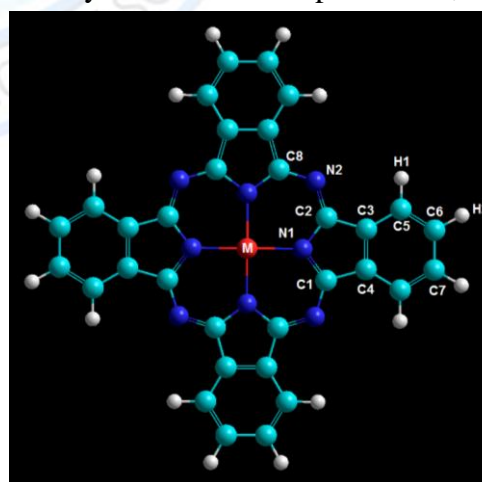
For transition metal complexes with several possible spin arrangements, a separate calculation within each spin multiplicity may be required to find the ground state of the complex.Concerning the multiplicity chosen throughout calculations, the d-block elements are trickiest. The multiplicity tends to become blurred when relativistic effects (spin-orbit coupling) are taken into account. In cases of unknown multiplicity, one has to try two or more options, each of which is a separate calculation. We tried values between (2-4) in this work.

Results & Discussion

Geometrical optimization:

The molecular structure of MPc is illustrated in (Figure-1) wherein the central metal (M) is coordinated to four N atoms. Full geometry optimization of each MPc is performed using MP3 method. The final geometry reached were D_{2h} for CoPc and NiPc, while it was D_{4h} for CuPc.

The D_{2h} symmetry constraints lead to structures that are very close to the expected D_{4h} symmetry^[19,20].The optimized bond lengths for the various MPc are collected in (Tables 1,2 and 3) for CoPc, NiPc and CuPc respectively. Experimental and more accurate Density Functional (DF) method results have been reported for comparison.From the first row, the metal–nitrogen distances (N_1 -M) in CoPc and CuPc were comparable to DF method results while it was more accurate for the closed-shell NiPc than the reported DF method results. Regarding the N_1 -C₁ bond length within the Pc ring, it is evident that PM3 method was unable to predict this bond length accurately as much as the rest of the bond lengths. The C₁-N₂ bond length, more distant from the metal, is less dependent upon the nature of the latter; even less sensitivity is observed in the other aspects of the Pc geometry.Theoretical results for the structural parameters of MPc from other authors are also



(Figure1) Atomic numbering scheme of MPc used in this work.

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listed in Table I for comparison. The geometries from those calculations are very similar to our own. Generally, the calculated geometry and all results are in good agreement with experimental and reported theoretical results.

(Table 1) calculated structural parameters for CoPc after geometrical optimization. Atom labels from Fig. 1. Experimental and theoretical data are reported for comparison.

Bond length (Å)	This work	Experimental ^(**)	DF method ^(*)
N ₁ -M	1.928	1.912	1.923
N ₁ -C ₁	1.442	-	-
N ₁ -C ₂	1.442	1.381	1.385
N ₂ -C ₂	1.347	1.317	1.322
N ₂ -C ₈	1.347	-	-
C ₁ -C ₄	1.446	-	-
C ₂ -C ₃	1.446	1.459	1.458
C ₃ -C ₄	1.419	1.403	1.459
C ₃ -C ₅	1.390	1.394	1.396
C ₅ -C ₆	1.394	1.401	1.399
C ₆ -C ₇	1.396	1.405	1.407
C-H (av.)	1.095	-	1.090

(Table 2) calculated structural parameters for NiPc after geometrical optimization. Atom labels from Fig. 1. Experimental and theoretical data are reported for comparison.

Bond length (Å)	This work	Experimental ^(**)	DF method ^(*)
N ₁ -M	1.897	1.830	1.923
N ₁ -C ₁	1.417	-	-
N ₁ -C ₂	1.417	1.380	1.384
N ₂ -C ₂	1.370	1.380	1.320
N ₂ -C ₈	1.328	-	-
C ₁ -C ₄	1.447	-	-
C ₂ -C ₃	1.447	1.460	1.455
C ₃ -C ₄	1.417	1.380	1.403
C ₃ -C ₅	1.389	1.390	1.397
C ₅ -C ₆	1.394	-	1.396
C ₆ -C ₇	1.396	-	1.410
C-H (av.)	1.095	-	1.090

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(Table 3) calculated structural parameters for CuPc after geometrical optimization. Atom labels from Fig. 1. Experimental and theoretical data are reported for comparison.

Bond length (Å)	This work	Experimental ^(**)	DF method ^(*)	DF method ^(***)
N ₁ -M	1.899	1.935	1.976	1.935
N ₁ -C ₁	1.429	-	-	-
N ₁ -C ₂	1.429	1.366	1.377	1.369
N ₂ -C ₂	1.368	1.328	1.328	1.317
N ₂ -C ₈	1.318	-	-	-
C ₁ -C ₄	1.435	-	-	-
C ₂ -C ₃	1.435	1.453	1.460	1.445
C ₃ -C ₄	1.416	1.400	1.409	1.400
C ₃ -C ₅	1.402	1.388	1.397	1.388
C ₅ -C ₆	1.381	1.377	1.396	1.390
C ₆ -C ₇	1.409	1.400	1.409	1.402
C-H (av.)	1.095	-	1.090	-

(*) Ref. (21), (**) Ref. (22), Ref. (23)

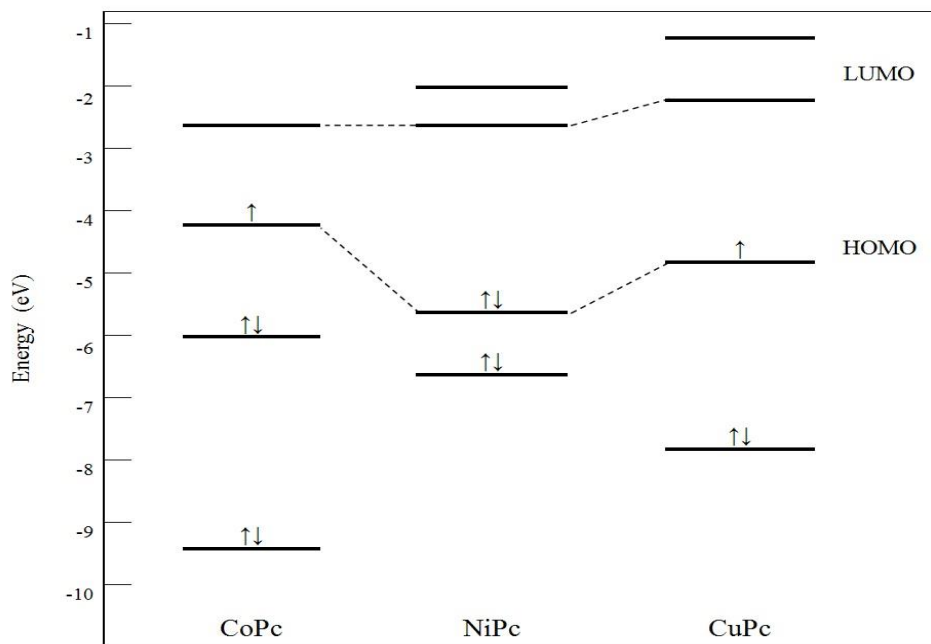
Electronic structure:

The optimized geometries of the three molecules were used in single point calculations to predict the electronic structure of the MPC's. Since ZINDO/S is parameterized to reproduce spectroscopic transitions, therefore it's not used for geometry optimization. However we obtained better results by performing a single-point calculation with ZINDO/S on the geometries obtained from the PM3 method.

For many MPC's, there exists no consistent picture of the electronic ground state. For example in CoPc, the divalent Co(II) ion is a $3d^7$ system with a possible $S = 1/2$ (low-spin) or $S = 3/2$ (high-spin) configuration. Charge density studies as well as theoretical calculations such as density functional theory (DFT) calculations hint toward a low-spin $S = 1/2$ situation.^[24,25]

We considered MPC's that are low-spin systems: CuPc, CoPc^[26] (open-shell systems) with $s = 1/2$ and CoPc (closed-shell system) with $s = 0$. The nature and energy position of some of the most chemically significant orbitals of CuPc, including the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were calculated and plotted three dimensionally. The orbitals are labeled according to the irreducible representation of D_{4h} . Under this point group, the five metal d orbitals transform as $a_{1g}(d_{z^2})$, $b_{1g}(d_{x^2-y^2})$, $e_g(d_{zx}, d_{yz})$, and $b_{2g}(d_{xy})$. Taking the molecule to lie in the xy plane, the d_{xz} , d_{yz} orbitals have p character and the rest may be considered of s type.

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(Figure 2) Orbital energy levels for selected outer molecular orbitals in the three MPC's.

Figure-2 illustrates the energies of (HOMO) and (LUMO) MOs for the ground states of the threeMPCs. The calculated electronic energy states are of reasonable accuracy.

The calculated energy gaps between the HOMO andLUMO of the three MPC's are displayed in (Table4).The main features of the electronic structure of closed-shell NiPc have been satisfactorily accounted for. However, ZINDO/S method showed less efficiency when dealing with open shell samples especially CoPc.PM3 and ZINDO/S do not use d-orbitals in their basis sets and therefore do not give very accurate results for most d-metal compounds nor for those main group elements where, from ab initio studies, d-orbitals are known to be of importance.

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(Table 4) Calculated energy gaps (eV) between HOMO and LUMO. Orbitals in brackets represent LUMO and HOMO, respectively.

MPc	Energy gap (LUMO,HOMO)	
	This work	DF results ^[22]
CoPc	1.455(a_{1g}, b_{2g})	1.96($1e_g, 2e_g$)
NiPc	3.10(a_{1u}, b_{1g})	1.47(a_{1u}, b_{1g})
CuPc	2.768(b_{1g}, b_{2g})	1.42($b_{1g}, 2e_g$)

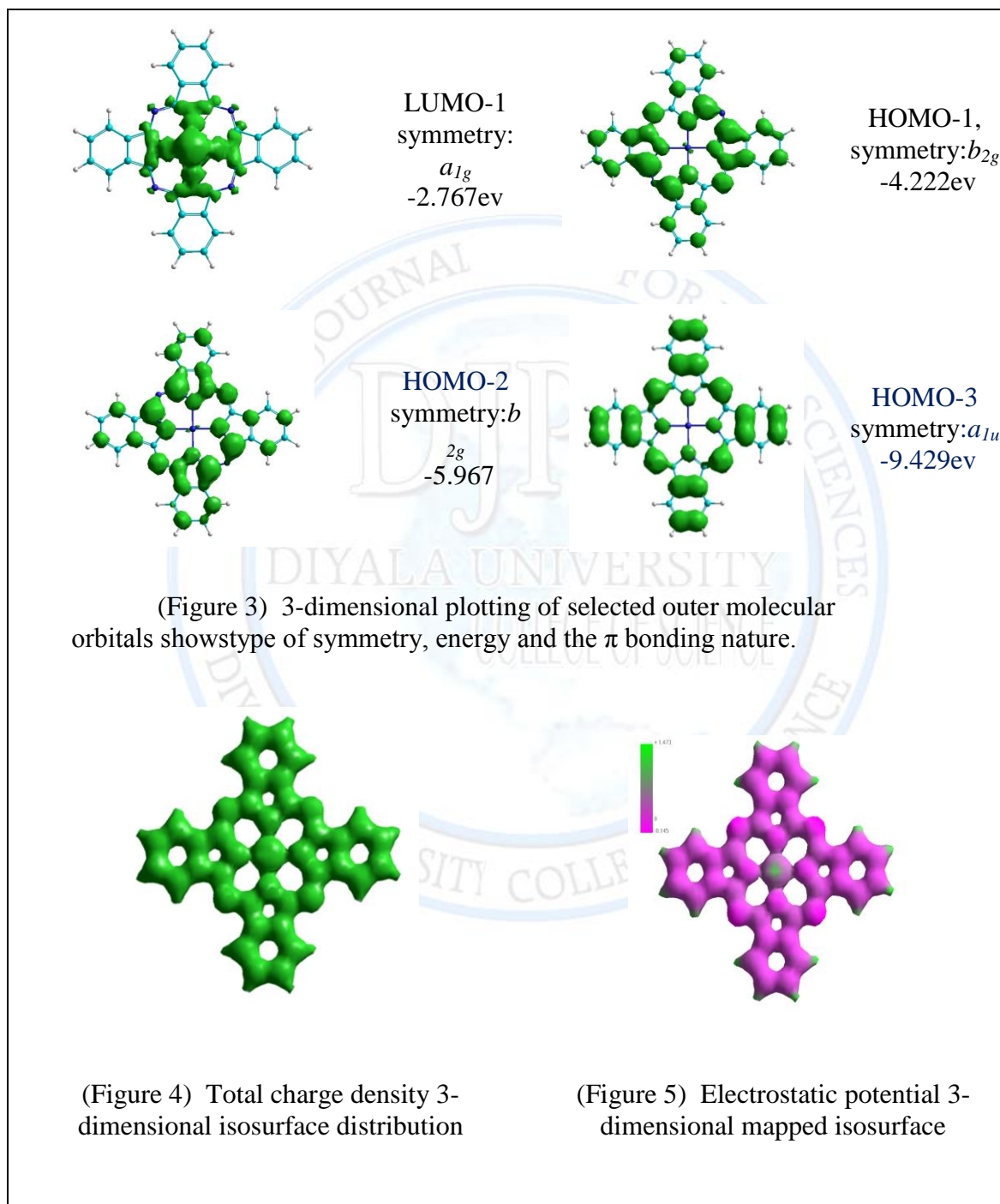
To notice the type of orbitals and electronic charge distribution within the three MPc's, some of the important orbitals were three dimensionally plotted. The results are shown in figures 3, 6 and 9 for CoPc, NiPc and CuPc respectively.

Also the total charge density 3-dimensional isosurface distributions were plotted. The attachment of the central metal with the four N atoms is clear. The results are shown in figures 4, 7 and 10 for CoPc, NiPc and CuPc respectively.

Moreover, the electrostatic potential 3-dimensional isosurfaces were mapped. This emphasizes why the H atoms can be replaced with different ligands. The results are shown in figures 5, 8 and 11 for CoPc, NiPc and CuPc respectively.

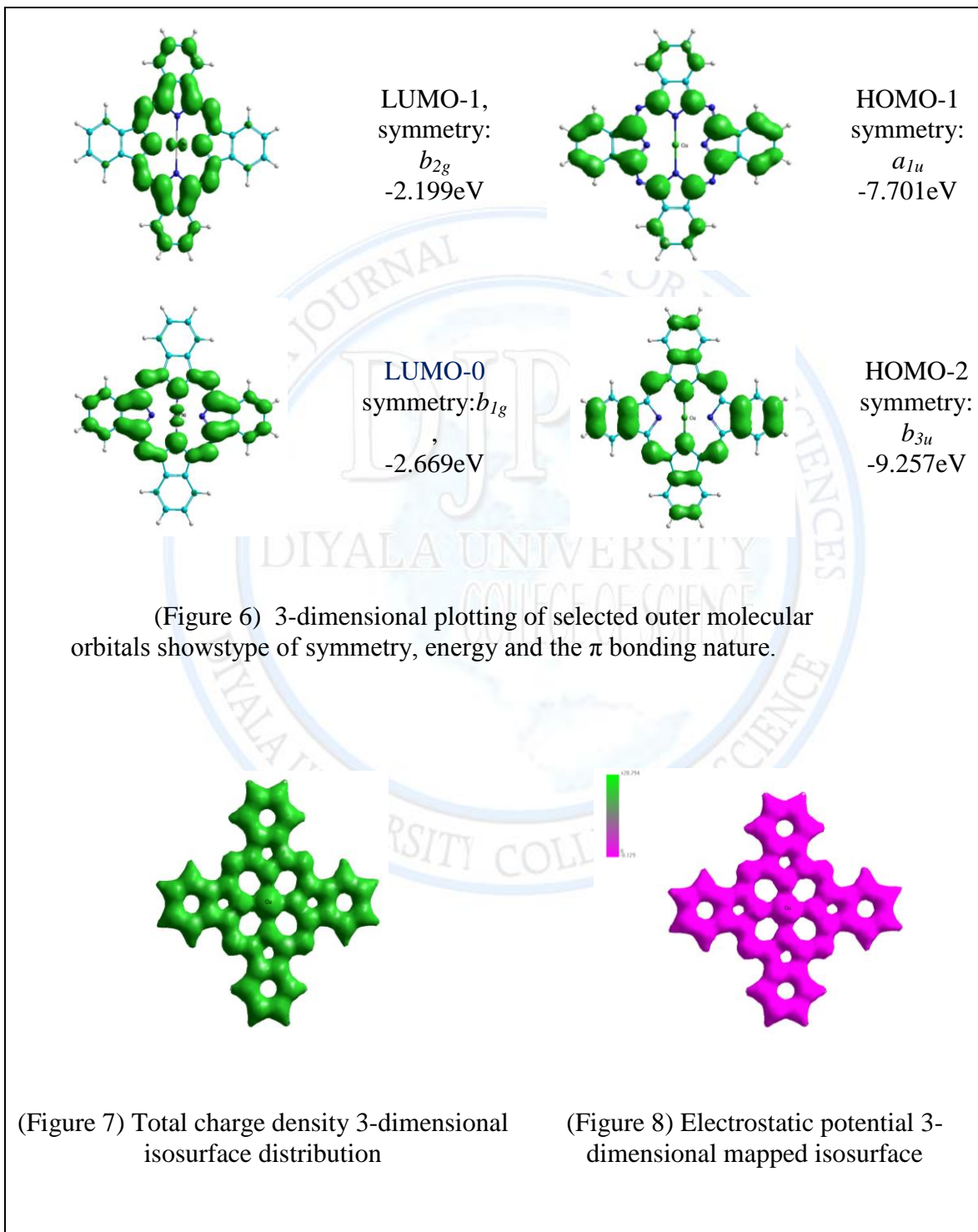
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Scheme of the chemical structure of CoPc molecule. The local symmetry around the central transition-metal ion is tetragonal (D_{2h} symmetry), where the molecule's z-axis points along the normal of the molecular plane.



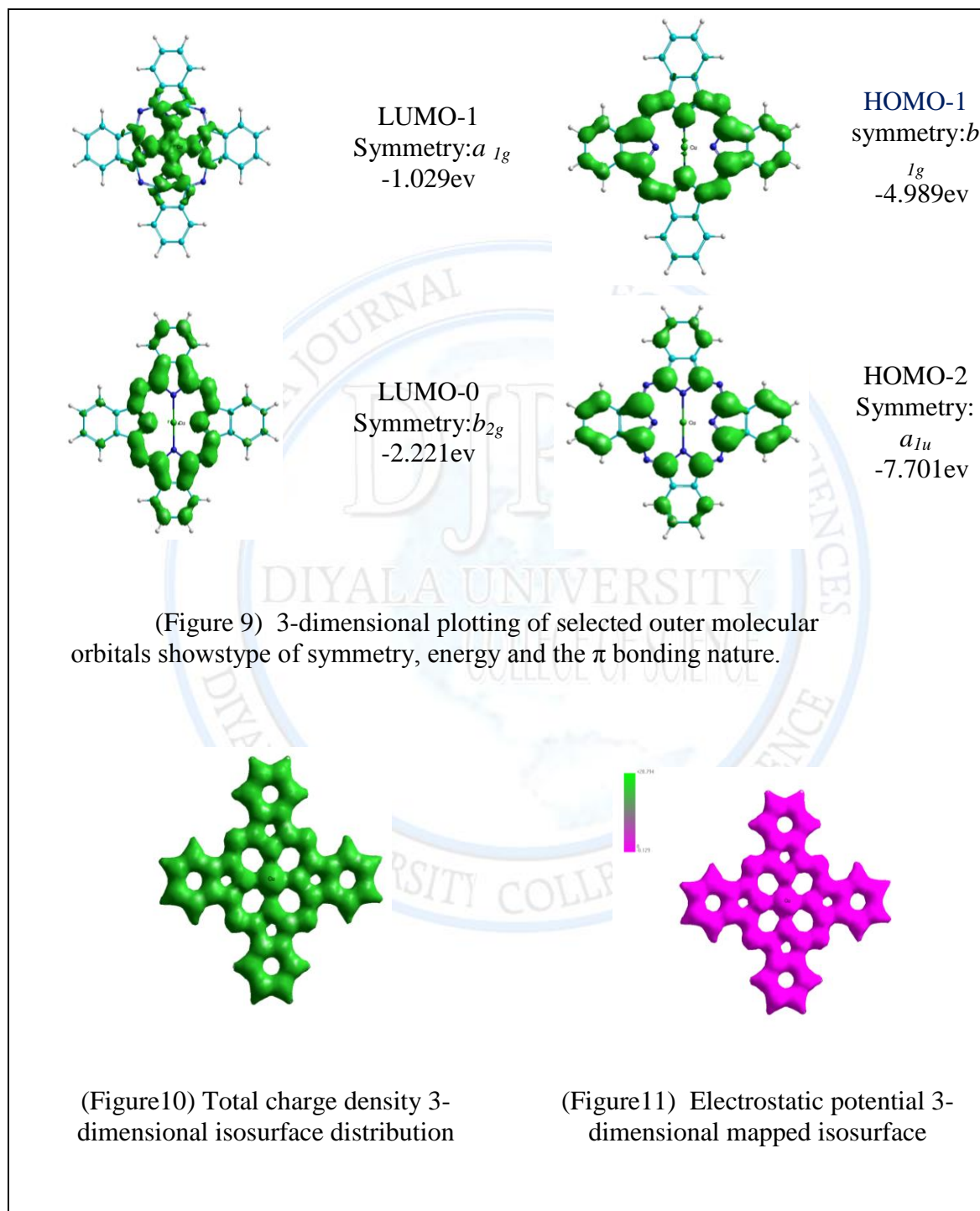
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Scheme of the chemical structure of NiPc molecule. The local symmetry around the central transition-metal ion is tetragonal (D_{4h} symmetry), where the molecule's z-axis points along the normal of the molecular plane.



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Scheme of the chemical structure of CuPc molecule. The local symmetry around the central transition-metal ion is tetragonal (D_{4h} symmetry), where the molecule's z-axis points along the normal of the molecular plane.



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