

## Study of the Electronic Properties of the Metallophthalocyanine as a Function of the Central Metal Atom

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### INTRODUCTION

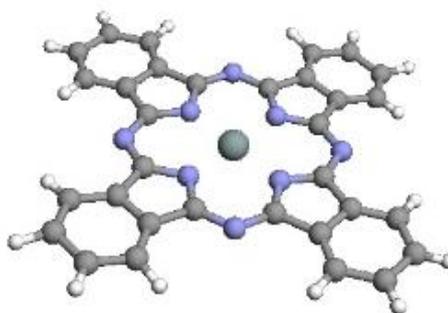
Phthalocyanines (Pcs) comprise a large class of compounds with many interesting properties. Several studies have addressed the impact of the position of the central metal atom relative to the organic cage of the phthalocyanine<sup>1</sup> and the possibility of exploiting it in numerous applications. Quite often, this central atom has *d* orbitals that may or may not interact with the  $\pi$  electron system of the molecule, thus contributing only to the geometrical properties or to the electronic properties of Pcs as well. Organic compounds, such as metallophthalocyanines have emerged as important candidates to be used as active materials in numerous applications such as, electrochromic display device, organic light emitting diodes (OLEDs) and organic photovoltaics (OPVs). Here, we analyze the effects of the metal on key properties of the molecule, such as the frontier orbital energies and first excitation energy ( $S_0 \rightarrow S_1$ ). These properties are key in the selection of which metallophthalocyanine should be used for particular technological applications making use of this interesting compound.

### METHODS

We started our study extracting phthalocyanines from the X-Ray coordinates available in the Cambridge Structural Database (CSD). With these geometries, we proceeded with the following steps: we added -H atoms in the cases where those atoms were missing; we replaced any saturated chains by -CH<sub>3</sub>. These adapted geometries were used in the following calculations: **i**) a TD-DFT calculation to compute vertical excitation energies ( $S_0 \rightarrow S_1$ ) using the original (X-Ray) geometry; **ii**) a Single Point calculation to compute the frontier orbital energies with the original (X-Ray) geometry; **iii**) a geometry optimization, followed by a Single Point and TD-DFT calculations to recompute the properties listed before for the optimized geometries.

### RESULTS AND DISCUSSION

We analyze the first absorbing excited state energy for the various molecules investigated in this study. We can conclude that the energy of this state in both the molecules have values next comparing the values obtained with X-Ray geometries and the optimized geometry. We show the orbital energies of the highest three occupied orbitals and lowest three unoccupied molecular orbitals, both using the X-Ray and optimized geometries. The HOMO→LUMO energy are very comparable in all the molecules studied.



**Figure 1.** Molecule of metallophthalocyanine

### CONCLUSIONS

In this study, we investigated the impact of the central atom on the electronic properties of phthalocyanines. These preliminary results show that the central atom can promote from little to major changes in the electronic properties of MePcs, depending on the interaction of its electronic structure with the  $\pi$  electron system of the Pc.

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<sup>1</sup> Ruan, C., Mastryukov, V., Fink, M., Journal of Chemical Physics, 111, 3035-3041 (1999).