

## Simulation of the electronic properties of Group 14 phthalocyanine derivatives

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### Abstract

The focus of this project is to apply computational materials chemistry approaches to understand the ambipolarity of charge transport in crystalline Group 14 phthalocyanines. Such molecular materials, which fall under the broader context of organic semiconductors, are of interest for next generation, flexible electronics applications. More specifically, the project will deploy theoretical simulations run in a high-performance computing environment to provide evidence that the dimensionality of charge transport in these materials can be finely tuned by substituting the phenoxy axial groups with fluorine atoms and by varying their number of positions. In this step of the data collection process, the theoretical simulations were used to compute the energy values for different variations of phthalocyanine, internal reorganization energies, Huang-Rhys parameters for hole transport, and the shapes of the molecular orbitals.

### Introduction

Organic photovoltaics (OPV) are a possible technology for large-scale deployment of renewable energy generation. They have the advantages of being more easily processed, using less material, and being more substrate-independent than traditional inorganic PVs such as silicon.<sup>1</sup> Of the common OPV materials, boron subphthalocyanine chloride is unusual for having a large molecular dipole moment. As opposed to the typically planar geometry of phthalocyanines, which consist of four fused diiminoisindole rings, boron subphthalocyanine chloride adopts an inverted umbrella shape with only three fused diiminoisindole rings. Previously, boron subphthalocyanine chloride has been shown to offer improved efficiency over

phthalocyanines, which previous experimental work attributes in part to molecular ordering at the

donor/accepter interface creating interfacial fields. This has also been observed in polar phthalocyanines. The structure of the boron subphthalocyanine chloride molecule, indicating the group-III metal and the halide sites. In this work, we use ab initio methods to computationally evaluate and identify useful derivatives of boron phthalocyanine chloride for OPV applications, where the boron and chlorine atoms are substituted for other trivalent elements and halogen atoms, respectively. These substitutions are chosen so as to have the greatest effect on the molecular dipole moment. The trivalent site elements explored in this work are boron, aluminum, gallium, indium, scandium, and yttrium. The halogen site elements used in this work are fluorine, chlorine, bromine, and iodine. Thus, a total of twenty-four molecules are examined in our simulation matrix. For the remainder of this paper, to designate a subphthalocyanine with a given pairing of trivalent element, T and halogen element, X, we use the abbreviation T-X. For example, B-Cl refers to the commonly described boron subphthalocyanine chloride. Of the molecules explored here, the B-F, BCl, and B-Br molecules have been observed experimentally and their crystal structures are known.<sup>4, 5</sup> In order to evaluate these concept molecules as OPV materials, the structure, as well as several electrical and optical properties, are calculated for each molecule both in the gas phase and in their predicted crystalline solid phases. Many of the molecules simulated in this work have thus far eluded synthesis,<sup>4, 34</sup> Therefore, by identifying the most promising candidates for a given application via the simulation-

based predictive 3 evaluation of molecular concepts, we hope to facilitate on-target materials selection and provide motivation for the development of the necessary synthesis routes. The B-Cl molecule is used to validate our electronic and optical properties calculations since its properties are known experimentally. The B-Cl compound forms a purple material with an optical bandgap of 2.0 – 2.1 eV.<sup>2, 4, 6</sup> The B-CL molecule also has interesting non-linear optical properties. The crystal structures of the B-F, B-Cl, and B-Br derivatives have been found using X-ray diffraction to be orthorhombic of space group Pnma, with each unit cell containing four molecules.<sup>5, 8</sup> All molecules have the shape of an inverted umbrella with a molecular dipole pointing from the electronegative halogen towards trivalent site. In the crystalline phase, there is no net polarization due to the alternating arrangement of molecular dipoles. The B-Cl unit cell viewed along the c direction (left) and b direction (right) rendered from Ref. 8. In both renderings, the a direction is horizontal. Properties of interest. For the gas-phase molecules, the relaxed geometry is used to compute the HOMO/LUMO relative to the vacuum level. These levels are crucial for band alignment in organic electronic device design. The A B 4 molecular dipole moments were also calculated from the relaxed geometry. The dipole moment of a molecule can play a significant role in electronic properties of interfaces.

## Conclusion

The atomic radius of the group 15 element is important for determining the Pc structure, so that this can be

controlled by the choice of group 15 elements. Electrochemical data revealed, while MO calculations suggested, that the red-shift of the Q-band is attributable to a decrease of the HOMO–LUMO gap due to significant and moderate stabilization of the LUMO and HOMO, respectively. The effect of peripheral substituents and a central P(V) ion on the Q-band shift was independently predicted by MO calculations, while the magnitude of the total calculated shift was in good agreement with the experimental observations. The combination of spectral, electrochemical, and theoretical considerations revealed that all of the central group 15 elements, peripheral group 16 elements, and their positions are necessary to shift the Q-band beyond 1000 nm, indicating that the substitution effects of group 15 and 16 elements act synergistically. The Pcs having Q-bands beyond 1000 nm in this study also had stability under aerobic conditions comparative to that of CuPc, which is presently being widely used in consumer products.

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