



# The effect of substitution on reorganization energy and charge mobility in metal free phthalocyanine

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## ABSTRACT

To gain insight into how the electronic properties of discotic organic materials may be modified through substitution, the reorganization energy and the charge mobility of metal free phthalocyanine, and of several mono-substituted derivatives, are studied by electronic structure methods. It is found that the reorganization energy of phthalocyanine is not significantly changed by substitution on an outer phenyl ring, but is more strongly influenced when the inner crown amine ring is substituted. The relationship between reorganization energy and substituent is studied through the use of; substituent constant, HOMO energy, and geometry relaxation. The computed charge mobility shows stronger relationship to coupling matrix element than reorganization energy. A hybrid computational screening method in which the reorganization energy is calculated at the DFT level and the coupling matrix element is calculated at the AM1 level shows good predicting power for trends in charge mobility at reduced computational expense.

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## 1. Introduction

Conducting organic materials have been of interest in recent years for developing lightweight, cheap, and flexible electronic devices, such as organic light-emitting diodes (OLED), data storage systems, field-effect transistors (FET), and solar cells [1–4]. The efficiency of such organic devices is usually governed by the charge mobility in the conducting organic material because mobility is the one of the important properties that defines the ability of a material to transport charge. The above-mentioned electronic devices require fast hole mobility ( $\sim 10 \text{ cm}^2/\text{V s}$ ), but most conducting organic materials have low mobility [1,5]. Many efforts have been made to improve the mobility in organic materials [3,4,6–13].

Recently, discotic materials, which consist of molecules having a conjugated disc-shape core [14], have been explored for use in optoelectronic devices because of their electronic properties [9,10]. These molecules are able to build up columnar molecular stacks due to maximal  $\pi$ -orbital overlap and pseudo-one-dimensional charge transfer between the conjugated cores of adjacent molecules in the stacked orientation [14]. Phthalocyanine is one such discotic material that has been considered. It has attractive electronic properties due to a small reorganization energy and a large coupling matrix element, as evinced by a large electronic splitting between the HOMO and HOMO–1 levels in the parallel dimer [11]. The role of the present study is to search for guidelines

for improving the electronic properties of discotic organic materials through the effect of substitution by studying the influence of substitution on the electronic properties of phthalocyanine.

## 2. Background

Given a molecular crystal, the charge hopping rate, which determines charge mobility in a non-adiabatic system, is usually assumed to be reliably approximated by Marcus–Hush theory. Eq. (1) expresses the hopping rate in the absence of an external electric field [1,5,6,10,12,15,16]

$$W = \frac{V^2}{\hbar} \left( \frac{\pi}{\lambda k_B T} \right)^{1/2} \exp \left( -\frac{\lambda}{4k_B T} \right). \quad (1)$$

Here  $V$  is the coupling matrix element,  $\lambda$  is reorganization energy,  $k$  is the Boltzmann constant,  $\hbar$  is the Planck constant, and  $T$  is Kelvin temperature. The coupling matrix element is dictated by the overlap of molecular orbitals on adjacent monomers, which is strongly dependent on the relative position and orientation of the neighboring molecules [1,6,10–12,17]. Reorganization energy reflects the geometry relaxation in a molecule when the electronic state changes. In the case of hole transport, the reorganization energy is expressed as

$$\lambda = E_+^* - E_+ + E^* - E, \quad (2)$$

where  $E_+$  and  $E$  are the energies at the optimized geometries for ionized and neutral species, respectively, and  $E_+^*$  and  $E^*$  are the energies

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of the ionic and neutral species at the optimized neutral and ionized geometries, respectively [1,10,15].

In the Marcus–Hush model, the charge transfer rate is governed by two parameters,  $V$  and  $\lambda$ , as shown in Eq. (1). These two parameters must be controlled to improve the mobility in organic materials. One possible way of increasing mobility is to control  $V$  by reconfiguring the molecular orientation in the organic material. For example, in the case of pentacene, the mobility for the amorphous material is  $10^{-2}$  cm<sup>2</sup>/Vs, but can be as high as 5 cm<sup>2</sup>/Vs in a thin film formed by vacuum deposition [3]. Another way to improve the mobility is to control reorganization energy. The reorganization energy of an organic material may be changed by changing the shape and size of the conjugated core through the use of a substituent [6–11,18–23]. The introduction of a substituent can also change the crystal structure, thereby altering the relative positions and orientations of the molecules in the crystal. Changing substituent can therefore be a very effective method to modulate electronic properties of organic materials because it can influence both parameters (reorganization energy and coupling matrix element), at the same time.

In this study, we calculated the reorganization energy of metal free phthalocyanine (H2Pc), and for comparison naphthalene, each with various substituents. The substituents can be divided into two categories, phenyl ring activating groups and phenyl ring deactivating groups. The reorganization energy responds differently to substitution by groups from these two categories. The reorganization energy is also influenced by substitution position. The relationship between reorganization energy and substituent is studied through the use of; substituent constant, HOMO energy, and geometry relaxation. We also calculated charge mobility of H2Pc and its substituted derivatives. The mobility shows stronger relationship to coupling matrix element than to reorganization energy.

### 3. Calculation method

The structures of H2Pc and naphthalene are shown in Fig. 1. There are two isomers of mono-substituted phthalocyanine, generated by substitution at position 1 or 2, because the presence of the two hydrogens on the inner crown amine ring removes the equivalence of the two positions. All initial and substituted structures of H2Pc and naphthalene were fully optimized using the GAMESS program [24]. Optimization was initially performed at the AM1 level, and then at the B3LYP/6-31G(d) level of theory [25,26]. This two-step optimization procedure is primarily to reduce overall computational expense, but also allows us to evaluate the predictive power of AM1. When reliable, AM1 can yield a substantial savings in computational expense and consequently extend the upper limit on size of systems that are computationally assessable; it is therefore useful to identify the extent of its applicability. To optimize ionized structures, the restricted open shell model was used for AM1 calculations and the unrestricted model for density functional theory calculations. (Restricted electronic structure models were used for all closed-shell species.) We calculated orbital contour maps of the HOMOs of H2Pc and naphthalene and their derivatives using Hyperchem version 6.02 [27]. The orbital contour maps of the HOMO and the HOMO–1 of various dimers were also calculated.

The amount of geometry relaxation  $\Delta r_{rms}$  due to bond length changes upon ionization of a molecule was quantified by a root mean square (RMS) method,

$$\Delta r_{rms} = \sqrt{\frac{1}{n_{bond}} \sum_i^{n_{bond}} (r_i^+ - r_i^0)^2}, \quad (3)$$

where  $r^+$  and  $r^0$  are bond lengths in the ionized and neutral geometries, respectively, and  $i$  is a bond number index.

Mobility calculations were based on idealized single-crystals of phthalocyanine and its mono-substituted derivatives. The initial crystal structure of unsubstituted phthalocyanine was built up using X-ray diffraction data [28] with Material Studio [29]. It was directly used for mobility calculation. To compare calculation methods, the crystal structure optimization of unsubstituted phthalocyanine employed first-principles total energy calculations based on density functional theory employing the local density approximation (LDA – Ceperly–Alder [30] and Perdew–Zunger parametrization [31]) and the generalized gradient approximation (GGA – Perdew–Burke–Ernzerhof parametrization [32]), as described in the review by Payne et al. and coded in the Cambridge serial total energy package (CASTEP) [33]. The electron–ion interactions were described by ultrasoft pseudopotentials [34]. A plane wave basis set with a cutoff energy of 260 eV was used to construct the (valence) electronic wave functions, which in combination with the choice of ultrasoft pseudopotentials gives well-converged energy differences. The cell volume increased slightly, about 2%, from that of the X-ray crystal structure, when optimized with LDA, but increased about 5% upon optimization with GGA. The stabilization energy is also slightly changed, less than 0.05% by LDA and less than 0.04% by GGA. These results suggest that LDA is reliable for optimization of phthalocyanine and imply that it should be adequate for substituted derivatives as well. Therefore, the crystal structures of its mono-substituted derivatives were generated computationally by substitution to H2Pc and subsequent optimization with Materials Studio [29]. The crystal structure optimizations for mono-substituted derivatives employed first-principles total energy calculations based on density functional theory employing the LDA under same parameters of unsubstituted H2Pc optimization.

Site energy differences for dimers with symmetry-inequivalent monomers were calculated by the effective fragment potential method [24]. The effective fragment potential for each neighbor molecule was created from the HF/STO-3G wavefunction of the neighbor.

## 4. Results and discussion

### 4.1. The effect of substitution on reorganization energy

The computed reorganization energy and geometry relaxation values for mono-substituted phthalocyanine and naphthalene are shown in Table 1. (All data in Table 1 were calculated at the DFT-B3LYP/6-31G(d) level.) The calculated reorganization energy of H2Pc is 0.043 eV, which is similar to that given in a previous DFT study by Tant et al. [11], who reported 0.045 eV using B3LYP with the (slightly more complete) 6-31(d,p) basis set. To quantify the degree of variation in reorganization energy with substituent position we define its root mean square (RMS) variation as

$$\Delta \lambda_{rms} = \sqrt{\frac{1}{n_{sub}} \sum_i^{n_{sub}} (\lambda_i - \lambda_h)^2}, \quad (4)$$

where  $\lambda_i$  and  $\lambda_h$  are the reorganization energies of mono-substituted and unsubstituted phthalocyanine, respectively,  $n_{sub}$  is the number of substituents considered and the index of summation runs over all substituents considered. The RMS values for H2Pc are different depending on the substituent position. When the substituent is at position 1 or 2, the reorganization energy of mono-substituted phthalocyanine does not change much compared to that of unsubstituted phthalocyanine. The RMS variations of reorganization energy are 0.0230 and 0.0282 eV, for

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