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Intrinsic dielectric properties of phthalocyanine crystals: An *ab initio* investigation

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Cu phthalocyanine (CuPc) based composites are expected to display high dielectric constants, of the order of several hundreds, based on recent experimental work. In an attempt to determine whether CuPc has a high dielectric constant intrinsically, and if so, in order to identify the circumstances under which such high dielectric constants could result, a systematic *ab initio* study is undertaken. This study extends prior work on the intrinsic dielectric properties of isolated CuPc and the closely related H_2 phthalocyanine (H_2Pc) monomers. The tendency of CuPc and H_2Pc monomers and polymeric sheets to stack is critically assessed, and the concomitant changes in the electronic and optical properties as a function of the stacking distance are determined. Our results indicate that both CuPc and H_2Pc systems exhibit an insulator to metal transition as the stacking distance approaches 3 Å (the equilibrium spacing). Consistent with this behavior, the dielectric constant reaches large values as the stacking distance approaches 3 Å, while it is small for larger stacking distances, in accord with our prior estimates.

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I. INTRODUCTION

Thin films of various organic semiconductors are currently investigated for electronic and photonic device applications. Characterized by long-range order in crystalline layers and chemical and thermal stability,[1] phthalocyanines are a class of promising materials for organic based transistors,[2,3] photovoltaic solar cells,[4,5] and gas sensors. Recently, copper phthalocyanine (CuPc) oligomers have been used as a filler to a polymer matrix to develop an all organic high dielectric constant composite.[6] However, it is unclear whether the resulting high dielectric constant is intrinsic to CuPc. In fact, it has recently been pointed out that several extrinsic factors could contribute to the observed large dielectric constant values.[7]

Our recent study has established an initial understanding of the dielectric properties of isolated phthalocyanine (Pc) based monomer molecules.[8,9] We have computed the dielectric constant of isolated CuPc monomers using both a semiclassical method[8] and a fully quantum-mechanical method[9] based on a recently developed theory of the local dielectric permittivity.[10] In both of these cases, the results reveal relatively low dielectric constants of isolated CuPc monomers: 15 along the plane and 2–3 perpendicular to the plane of the monomer, considerably lower than the value of several hundreds reported for CuPc-polymer composites.[6,8,9]

In this contribution, we present a systematic study of structural, electronic, and dielectric properties of vertical stacks of CuPc and H_2Pc monomers and sheets, based on density-functional theory (DFT). The primary motivation for studying the stacked variety of monomeric and polymeric sheets of CuPc and H_2Pc is twofold. Firstly, this would serve as an extension to our prior work that dealt with purely isolated monomeric Pc systems and could help explore other situations in which large dielectric constants can be expected; and secondly, porphyrins (including Pc molecules) are known to oligomerize and stack, whenever possible, during synthesis.[11,12] For instance, it has recently been shown that H_2Pc, when grown layer by layer, tends to stack up vertically (normal to its plane) rather than adopt the monoclinic α or β phases, which are stable in bulk systems.[13] While CuPc systems are most relevant from an application point of view, we consider H_2Pc in order to estimate the role played by Cu.

We begin by demonstrating that monomeric and polymeric CuPc and H_2Pc display a strong tendency to stack. Analysis of the electronic structure of these systems indicates that a transition from insulating to metallic behavior results as the stacking distance decreases and approaches the equilibrium stacking distance. We then determine the dielectric constant as a function of the stacking distance via first-order perturbation theory. We find that for large stacking distances,

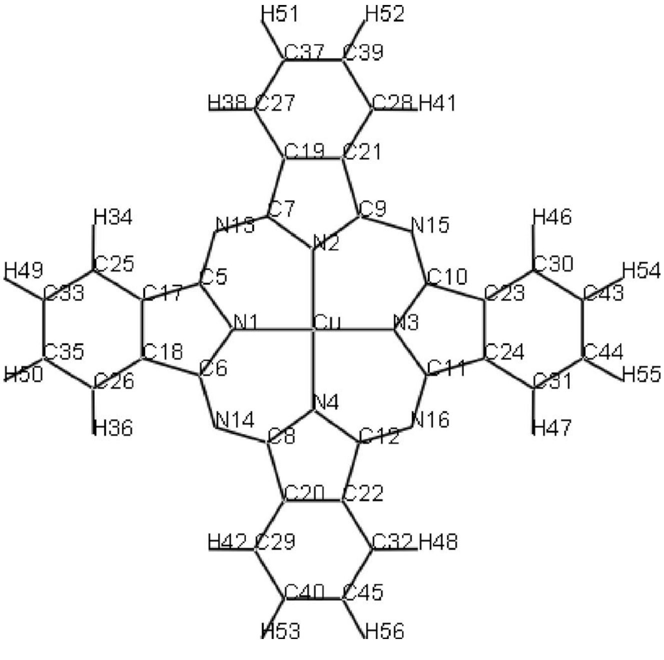

FIG. 1. Atomic structure of the CuPc molecule. In H_2Pc, the two H atoms are bound to N^1 and N^3.

TABLE I. Calculated structural parameters of H_2Pc, MgPc, and CuPc; the atomic numbering scheme of Fig. 1 is used. Experimental values (Ref. 16) of CuPc are shown in parentheses. All bond lengths are in Å and bond angles in degrees.

Parameter	H_2Pc	CuPc
H-N^1	1.045	
Cu-N^1		1.956 (1.935)
N^1-C^5	1.376	1.376 (1.366)
C^5-N^{13}	1.319	1.326 (1.328)
C^5-C^{17}	1.455	1.462 (1.453)
C^{17}-C^{18}	1.418	1.413 (1.400)
C^{17}-C^{25}	1.405	1.404 (1.388)
C^{25}-C^{33}	1.402	1.404 (1.377)
C^{33}-C^{35}	1.418	1.417 (1.413)
C^5-N^1-C^6	111.77	108.47 (107.3)
N^1-C^5-N^{13}	127.95	128.07 (127.6)
N^1-C^5-C^{17}	106.90	109.48 (110.4)
C^5-N^{13}-C^7	122.36	122.32 (122.2)
C^5-C^{17}-C^{18}	107.21	106.28 (106.0)
C^{18}-C^{17}-C^{25}	121.38	121.51 (121.1)
C^{17}-C^{25}-C^{33}	117.19	117.06 (117.9)
C^{25}-C^{33}-C^{35}	121.43	121.43 (121.0)

the computed dielectric constant is consistent with our previous estimates for isolated monomeric Pc molecules, while close to the equilibrium stacking distance, the dielectric constant displays large values, as well as singularities consistent with metallic behavior. All conclusions are qualitatively similar for both CuPc and H_2Pc, indicating that the dielectric properties of these systems are independent of the central atom(s).

The paper is organized as follows. In Sec. II, the computational methods specific to this work are described. In Sec. III, we present our analysis of the tendency of CuPc and H_2Pc systems to stack, their band structures, and frequency-dependent dielectric functions as a function of stacking distance. The dielectric constant intrinsic to Pc systems are extracted from these results and compared to available theoretical and experimental data. Conclusions are summarized in Sec. IV.

II. COMPUTATIONAL METHODS

All calculations presented here were performed using the local-density approximation (LDA) within DFT,[14] as implemented in the local orbital SIESTA code.[15] Norm-conserving nonlocal pseudopotentials of the Troullier-Martins type were used to describe all the elements. Atomic configurations of $[He]2s^22p^2$, $[He]2s^22p^3$, and $[Ar]3d^{10}4s^1$ were used for the C, N, and Cu pseudopotentials, respectively. The geometry of all cases considered were optimized such that each of the atomic forces was smaller than 0.04 eV/Å.

Figure 1 shows the structure of the CuPc monomer molecule, and Table I shows the values of selected optimized geometric parameters that characterize the structures of CuPc and H_2Pc, as determined here, along with available experimental data.[16] Our computed values are in excellent agreement with experiments and prior computations.[8,17,18]

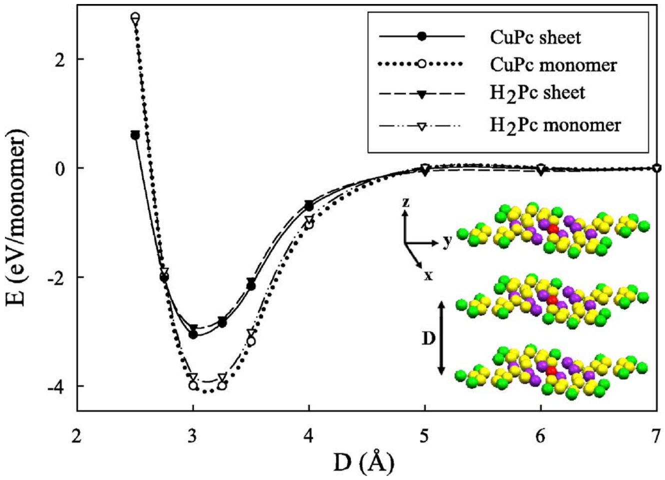

FIG. 2. (Color online) Total energy of stacked CuPc and H_2Pc monomers and sheets as a function of interlayer distance D. Regardless of the specific system, a stacking distance D of about 3 Å is preferred. Inset shows a vertical stack of CuPc monomers. Cu atom is in red, N in purple, C in yellow, and H in green.

The stacked CuPc monomer structure is illustrated in the inset of Fig. 2. The supercell with dimensions of 30×30 Å^2 in the x-y plane, when replicated in three dimensions, results in a one-dimensional chain of CuPc monomers along the z direction, with each monomer separated from its neighbors by a distance D. The monomers are separated well from the image monomers along the x-y plane by more than 15 Å. Analogous structures were considered for the H_2Pc case as well. Stacks of polymeric sheets of CuPc and H_2Pc were constructed by periodically repeating the planar molecule within the supercells of dimensions of 10.7221×10.7221 Å^2 and 10.669×10.7221 Å^2 in the x-y plane, and sheets are separated in the z direction by a distance D, resulting in stacked sheet structures.

The optical or electronic part of the dielectric function was computed using first-order perturbation theory.[14] The electronic wave functions and eigenvalues obtained from supercell DFT calculations of stacks of CuPc and H_2Pc monomers and sheets were used to determine the imaginary part of the energy (E)-dependent dielectric function $\epsilon_{imag}(E)$ using the relation[19–21]

$$\epsilon_{imag}(E) = \frac{e^2h^6}{2\pi m^2E^2}\sum_{ij}\frac{2}{(2\pi)^3}\int_{BZ} d\mathbf{k}|M_{ij}(\mathbf{k})|^2\delta[E - E_{ij}(\mathbf{k})], \tag{1}$$

where e, m, and h are the electronic charge, electronic mass, and Planck's constant, respectively. M_{ij} is a matrix element given by $\langle\psi_i(\mathbf{k})|\mathbf{e}\cdot\mathbf{p}|\psi_j(\mathbf{k})\rangle$, with $\mathbf{e}$, $\mathbf{p}$, and $\mathbf{k}$ being the polarization vector, momentum operator, and a point in reciprocal space, respectively, and ψ_i is the wave function. $E_{ij}=E_j-E_i$, where E_i is an eigenenergy. The integration in the above equation is performed over the first Brillouin zone (BZ). The real part of the dielectric function is obtained from the imaginary part by performing a Kramers-Kronig transformation.[14]

Only the electronic part of the dielectric function was computed in this work. This decision to consider just the electronic contribution was motivated by the fact that over 99% of the polarizability of CuPc and H_2Pc is electronic in origin.[8]

III. RESULTS AND DISCUSSION

A. Equilibrium stacking

The total energy of CuPc and H_2Pc monomers and sheets as a function of stacking distance D is shown in Fig. 2. It can be seen that at a stacking distance of 3 Å, both the stacked CuPc and H_2Pc monomers and sheets have the lowest total energy. The stacking energy is around 3 eV for CuPc and H_2Pc sheets and about 4 eV for CuPc and H_2Pc monomers. Our results for H_2Pc are nearly identical to those reported in a prior computational work.[13] These results indicate that a stacking distance of about 3 Å is strongly preferred, regardless of the nature of the Pc system (monomeric or polymeric) and the stacking energy is independent of the nature of the central atoms (Cu or H_2). These results are consistent with the equilibrium stacking distance of about 3–4 Å in the case of discotic systems in general[22,23] and of 3–3.5 Å in the case of various Pc systems.[13,24,25]

B. Electronic structure

The LDA band structures for stacked CuPc and H_2Pc are plotted in Figs. 3 and 4. The calculated bands are plotted along high-symmetry directions in the irreducible part of the Brillouin zone with the zero of energy corresponding to the Fermi energy. The band structures are dependent on the stacking distance and the inclusion of copper atoms and whether the system is monomeric or polymeric. It is worth mentioning that the LDA is known to underestimate the band gaps of insulator and [highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gaps of molecules]. Nevertheless, the trends that would result from this work are expected to provide important insights concerning this system.

The main features of the stacked CuPc and H_2Pc monomeric systems (Fig. 3) will be discussed first. For a stacking distance of 5 Å, the band structure shows no dispersion, indicative of discrete states corresponding to isolated molecules. The band gap (or more precisely, the HOMO-LUMO gap) in this case is about 1.09 eV for majority-spin electron and 1.5 eV for minority-spin electrons in the case of CuPc, and about 1.47 eV for H_2Pc. However, for both CuPc and H_2Pc stacked monomers with stacking distance of 3 Å, the band structures exhibit dispersion, resulting in the disappearance of the band gap. One notes particularly the band with hardly any dispersion around the Fermi energy for stacked CuPc monomer; analysis of the projected density of states indicates that this band has essentially a Cu 3d character.

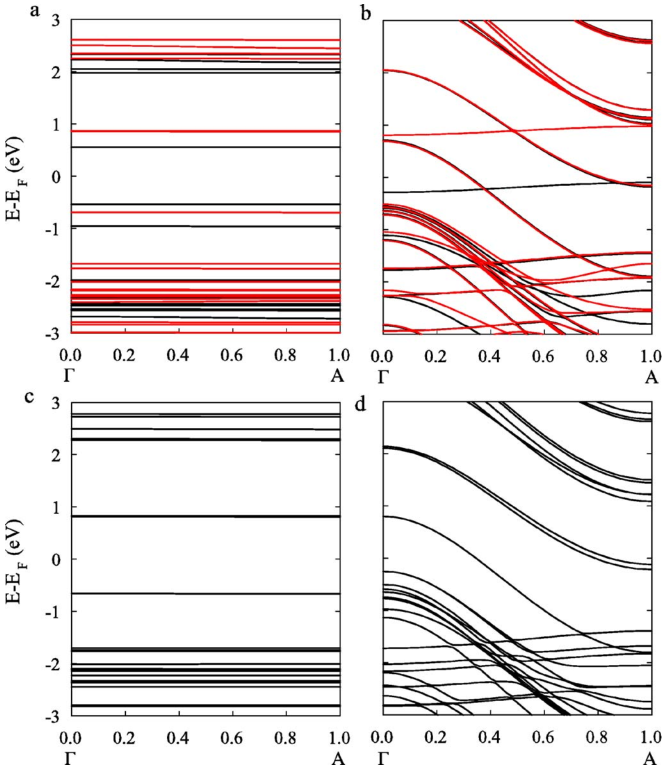

FIG. 3. (Color online) Band structure of stacked CuPc and H_2Pc monomers for two choices of the stacking distance D. (a) CuPc with $D=5$ Å, (b) CuPc with $D=3$ Å, (c) H_2Pc with $D=5$ Å, and (d) H_2Pc with $D=3$ Å. E_F represents the Fermi energy. In (a) and (b), the black and red lines represent majority- and minority-spin electrons. For $D=5$ Å, both systems display discrete states with a nonzero band gap (or HOMO-LUMO gap), while for $D=3$ Å, significant dispersion in the bands accompanied by the vanishing of the band gap can be seen, signaling the onset of metallic behavior.

In the case of stacked CuPc and H_2Pc sheets (Fig. 4) with stacking distance of 7 Å, the band gap is nonzero (about 0.5 eV for CuPc and about 0.3 eV for H_2Pc), while at a stacking distance of 3 Å, the bands exhibit dispersion along the direction from the Γ point to the A point, again resulting in the disappearance of the band gap. The Cu 3d states also contribute to the bands for the stacked CuPc sheets close to the Fermi energy.

The crystal-field splitting of the Cu d levels due to the fourfold symmetry at the center of a phthalocyanine molecule was explored for the case of CuPc sheets with $D=7$ Å. Figure 4(f) shows the projected density of states for Cu 3d_{z^2}, Cu 3d_{yz}, Cu 3d_{xz}, Cu 3d_{xy}, and Cu 3$d_{x^2-y^2}$ orbitals. Owing to symmetry, the d_{z^2} orbital does not interact with the Pc levels. The single d_{z^2} peak of Fig. 4(f) reflects this lack of interaction. The d_{xy} and $d_{x^2-y^2}$ orbitals are oriented most favorably for hybridization with a suitable Pc level with appropriate symmetry and energy. The three peaks with significant contributions from the d_{xy} and $d_{x^2-y^2}$ levels of Fig. 4(f) and the significant splitting of these levels indicate the strong interaction with Pc. The d_{yz} and d_{xz} levels are also oriented to allow for interaction with the Pc levels, but the degree of interaction is expected to be lower than that of the d_{xy} and $d_{x^2-y^2}$ levels. Hence, the splitting of levels with significant contributions from the d_{xz} and d_{yz} levels is not as significant.

The discussion so far indicates that while the band gap for both CuPc and H_2Pc stacked monomers and sheets is non-

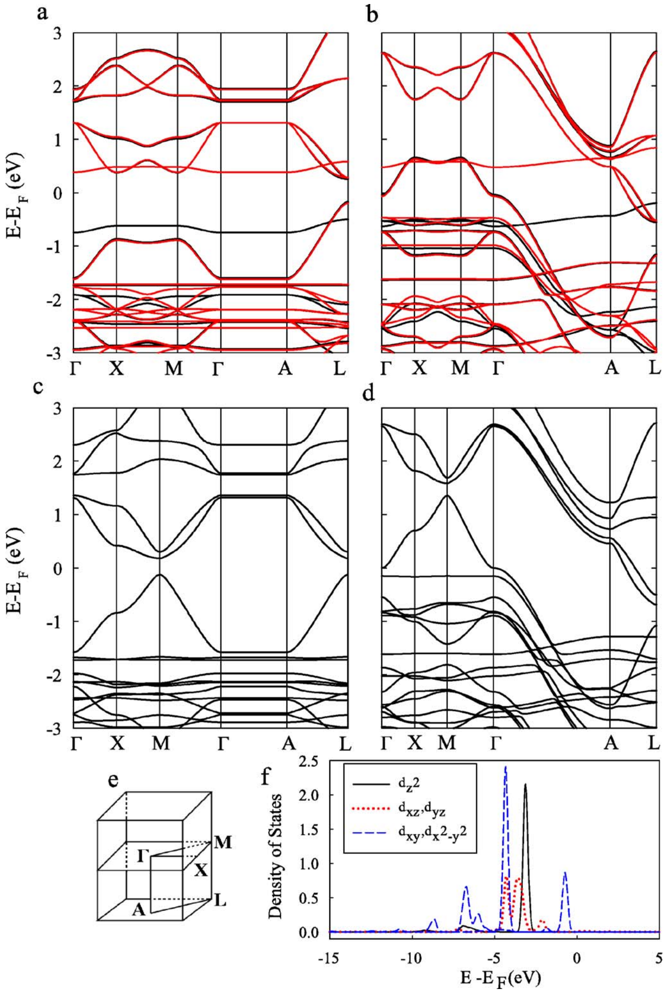

FIG. 4. (Color online) Band structure of stacked CuPc and H_2Pc sheets for two choices of the stacking distance D. (a) CuPc with $D=7$ Å, (b) CuPc with $D=3$ Å, (c) H_2Pc with $D=5$ Å, (d) H_2Pc with $D=3$ Å, (e) the first Brillouin zone (IBZ) and the special points within the irreducible wedge of the IBZ, and (f) projected density of states in CuPc sheets with $D=7$ Å, highlighting the contribution of Cu d orbitals. E_F represents the Fermi energy. In (a) and (b), the black and red lines represent majority- and minority-spin electrons. For $D=7$ Å, both systems display a nonzero band gap, while for $D=3$ Å, significant changes in the bands accompanied by the vanishing of the band gap can be seen, signaling the onset of metallic behavior.

zero for large stacking distance, the band gap is negligible at the equilibrium stacking distance of 3 Å. The variation of the band gap with respect to the stacking distance D has also been studied for several values of D. Figure 5 shows that the band gap significantly decreases with decreasing D for all cases, signaling an insulator to metal transition as the stacking distance is decreased. This low band gap is consistent with the high carrier hopping between layers, observed in discotic systems.[22,23] A further important implication of the insulator to metal transition is that the metallic behavior at small stacking distances could possibly manifest as large dielectric constants, as will be discussed below.

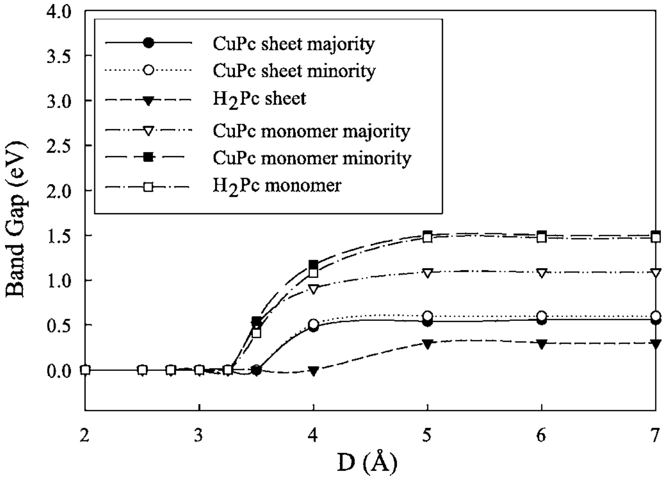

FIG. 5. Band gap of stacked CuPc and H_2Pc monomers and sheets as a function of stacking distance D. An insulator to metal transition occurs as D decreases and approaches the equilibrium stacking distance of 3 Å.

C. Dielectric properties of polymeric sheets

We can obtain further insight into the electronic structures by studying the optical properties. The dielectric functions of the CuPc and H_2Pc stacked sheets have been computed both along the plane of the CuPc and H_2Pc sheets (i.e., the x-y plane) and perpendicular to the plane (i.e., along the z direction), as a function of the stacking distance D. Below, we separately consider the dielectric function along each direction.

1. Dielectric constant along the CuPc plane

The real and imaginary parts of the dielectric function along the CuPc plane are depicted in Fig. 6 for a range of D values. Note that both CuPc sheets and the intervening vacuum contribute to the dielectric function. Thus, this system can be considered as a CuPc-vacuum "composite," and we refer to its dielectric function as $\epsilon^{||}_{composite}$ for stacked CuPc sheets. Consistent with this view, the dielectric function changes monotonically as the interlayer stacking distance D decreases. The behavior is systematic until a D value of about 3.5 Å is reached, but below 3.5 Å, the dielectric function displays singularities. We pay special attention to the values of the y intercept of the dielectric function, which we denote as $\epsilon^{||}_0$, and refer to as the dielectric constant henceforth. As can be seen from Fig. 6, while $\epsilon^{||}_0$ is purely real (displaying a systematic increase for decreasing D), for D >3.5 Å, it becomes complex, with a large real value for smaller values of D, similar to the behavior of a "lossy" metal. This is consistent with the vanishing of the band gap as the equilibrium stacking distance is approached (Fig. 5).

We can further extract the dielectric constant of the CuPc sheet itself from that of the composite using appropriate electromagnetic mixing theorems.[26] Several different mixing rules have been proposed to treat different cases of the configuration of the components of the composite. Of these, the two "ordered" configurations, namely, when the components are arranged in layers either parallel or perpendicular to the

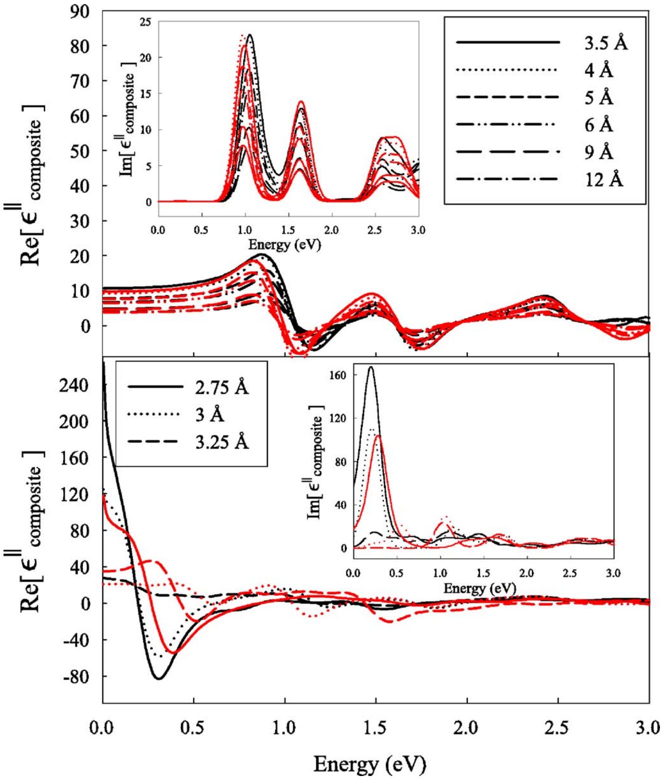

FIG. 6. (Color online) Dielectric function along CuPc and H_2Pc plane of stacked polymeric sheets. The real part of the dielectric function is shown for various choices of the stacking distance D, and the imaginary part is shown in the inset. Results for CuPc and H_2Pc are shown in black and red, respectively. For large D, the dielectric function is real at small energies and increases monotonically with increasing D. As the equilibrium spacing of 3 Å is approached, the dielectric function at small energies becomes complex, with the real part reaching large values.

electric field direction, provide the upper and lower bounds of the composite effective dielectric constant. These parallel and perpendicular situations are the most appropriate for the present work, as our composite is an ordered multilayer stack of CuPc (or H_2Pc) and vacuum.

The mixing rule that deals with the parallel component of the dielectric constant for our system results in the relation [9,26]

$$\epsilon_0^{\|} = \epsilon_{\mathrm{CuPc}}^{\|} d_{\mathrm{CuPc}}/D + \epsilon_{vac} d_{vac}/D, \tag{2}$$

where d_{CuPc} and d_{vac} are the thicknesses of the CuPc and vacuum regions, respectively, along the z direction (with $d_{\mathrm{CuPc}}+d_{vac}=D$), and $\epsilon_{\mathrm{CuPc}}^{\|}$ and ϵ_{vac} are their respective dielectric constants normal to the stacking direction. With $\epsilon_{vac}=1$ in our composite systems, the above equation reduces to

$$\epsilon_0^{\|} = \frac{(\epsilon_{\mathrm{CuPc}}^{\|}-1)d_{\mathrm{CuPc}}}{D} + 1. \tag{3}$$

Figure 7 shows a plot of $\epsilon_0^{\|}$ values versus 1/D. Indeed, a linear relationship between these two quantities with an intercept of 1 was obtained for large D values, as required by the above equation. If we make the further assumption that

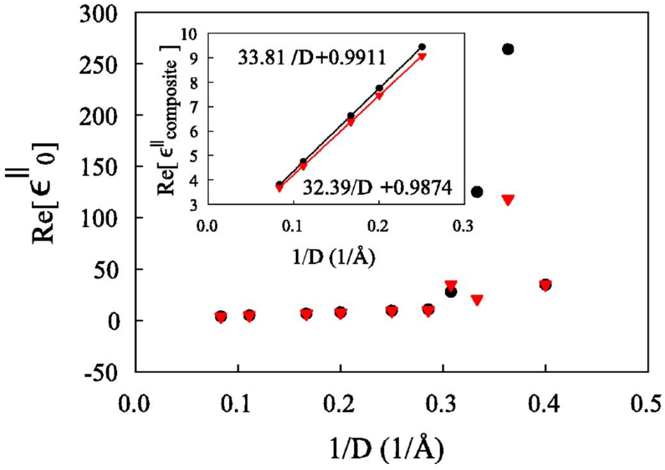

FIG. 7. (Color online) Planar component of the dielectric constant of stacked CuPc and H_2Pc sheet-vacuum composite vs$1/D$. The y intercept of the real part of the dielectric function from Fig. 6 is plotted for the entire range of D values studied. Results for CuPc and H_2Pc are shown in black dots and red triangles, respectively. The inset shows the same results but in the regime of large D from 4 — 12 Å. The linear fit of the data in the large D regime is in good agreement with that predicted by Eq. (3), indicating that the parallel capacitor model provides an adequate description.

$d_{\mathrm{CuPc}} \approx 3$ Å (the equilibrium D spacing), the slope of the linear fit of the inset of Fig. 7 [given as $(\epsilon_{\mathrm{CuPc}}^{\|}-1)d_{\mathrm{CuPc}}$] yields the in-plane dielectric constant of the CuPc as ≈13, consistent with our prior estimate.[8,9]

2. Dielectric constant perpendicular to the CuPc plane

A similar analysis has been carried out for the dielectric constant perpendicular to the CuPc plane. Both the real and imaginary parts of the dielectric function along the stacking direction, shown in Fig. 8, are found to vary with the interlayer distance D similar to the previous case. For D greater than 3.25 Å, the composite dielectric constant (i.e., the y intercept) decreases systematically and monotonically with D, but for smaller values of D, the dielectric constant increases abruptly. This picture is again consistent with the onset of "metallic" behavior as the equilibrium interlayer spacing is approached.

The dielectric constant perpendicular to the CuPc sheet itself ($\epsilon_{\mathrm{CuPc}}^{\perp}$) was obtained from the calculated dielectric constant of the CuPc-vacuum composite ($\epsilon_0^{\perp}$). In this case, the lower bound of the mixing rules that deal with layers of components stacked along the field direction must be used.[26,9] This results in

$$D/\epsilon_0^{\perp} = d_{\mathrm{CuPc}}/\epsilon_{\mathrm{CuPc}}^{\perp} + d_{vac}/\epsilon_{vac}, \tag{4}$$

where $\epsilon_{\mathrm{CuPc}}^{\perp}$ and ϵ_{vac} are the dielectric constants normal to the stacking direction of CuPc and vacuum, respectively. Simplifying as before, we get

$$1/\epsilon_0^{\perp} = \frac{(1/\epsilon_{\mathrm{CuPc}}^{\perp}-1)d_{\mathrm{CuPc}}}{D} + 1. \tag{5}$$

The behavior of $\epsilon_0^{\perp}$ in Fig. 9 demonstrates the linear relation between $1/\epsilon_0^{\perp}$ and $1/D$ as expected, with a y intercept of 1 in

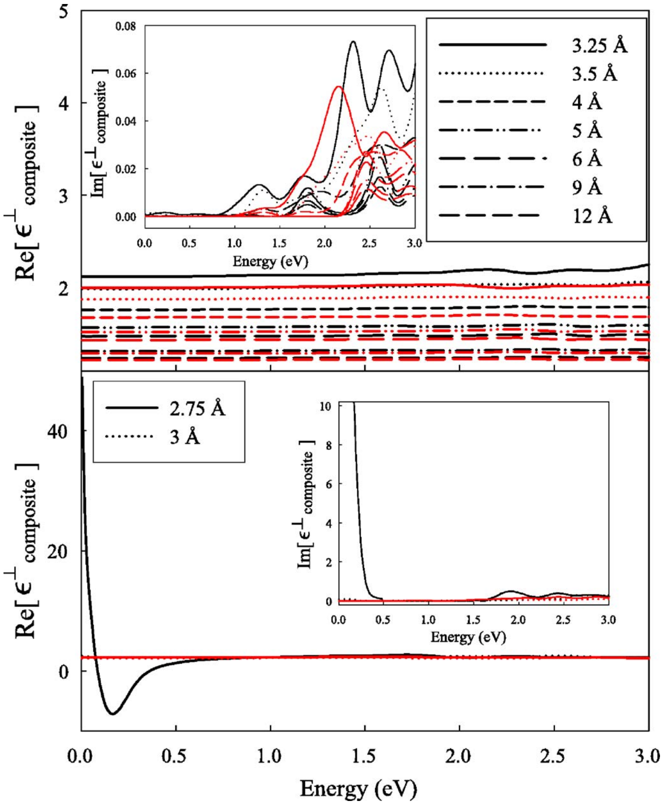

FIG. 8. (Color online) Dielectric function perpendicular to CuPc and H_2Pc plane of stacked polymeric sheets. The real part of the dielectric function is shown for various choices of the stacking distance D, and the imaginary part is shown in the inset. Results for CuPc and H_2Pc are shown in black dots and red triangels, respectively. For large D, the dielectric function is real at small energies and increases monotonically with increasing D. As the equilibrium spacing of 3 Å is approached, the dielectric function at small energies becomes complex, with the real part reaching large values.

a regime of larger vacuum thickness D. We derived an estimate of 1.9 for $\epsilon_{\mathrm{CuPc}}^{\perp}$ from the slope, again in accord with our previous estimates.[8,9]

3. Dielectric constant of stacked $\mathbf{H_2Pc}$ *sheets*

To investigate the role of copper atoms in CuPc sheets and get a more complete picture of the dielectric properties of phthalocyanine molecules, the dielectric properties of stacked H_2Pc sheet composites were studied. The relevant plots of the dielectric functions along the parallel and perpendicular directions, as well as the linear fits to extract the H_2Pc dielectric constants are shown in red plots in Figs. 6–9, following a procedure identical to that adopted for the CuPc case. All the H_2Pc results are qualitatively similar to those of the CuPc case. When the stacking distance D is small and close to 3 Å, the dielectric function at small energies is complex and large. In the larger D spacing regime, the dielectric constants of H_2Pc sheets were evaluated as 12 and 1.9, respectively, along the parallel and perpendicular directions. These results indicate that the role played by copper atoms is minor.

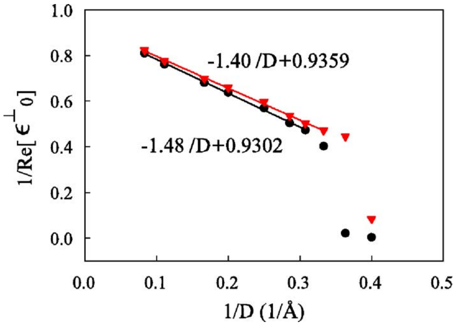

FIG. 9. (Color online) Perpendicular component of the dielectric constant of stacked CuPc and H_2Pc sheet-vacuum composite vs $1/D$. The y intercept of the real part of the dielectric function from Fig. 8 is plotted for the entire range of D values studied. Results for CuPc and H_2Pc are shown in black and red, respectively. The linear fit of the data in the large D regime is in good agreement with that predicted by Eq. (5), indicating that the series capacitor model provides an adequate description.

It is difficult to make a direct connection between our work and experiments, largely due to the unavailability of experimental data concerning dielectric functions for stacked Pc systems. Nevertheless, we note that our dielectric function results for H_2Pc with stacking distances close to the equilibrium spacing is in qualitative agreement with recent experimental work on thin films of H_2Pc in the monoclinic α phase.[28] Alamri *et al.* report the optical dielectric function (which presumably is averaged along all directions) in the 1–6 eV photon energy range. Although the α phase is considerably different from the situation considered here, it is interesting to note that their dielectric function displays peaks and a value of about 5 at 1 eV, close to our predictions (Fig. 6).

IV. SUMMARY

In summary, we have performed a density-functional theory based study of the tendency of CuPc and H_2Pc monomers and polymeric sheets to stack vertically (normal to the plane of molecules) and determined the accompanying changes in the electronic and dielectric properties. This study was motivated by a need to estimate the intrinsic dielectric constant of phthalocyanine based systems and to develop an understanding of the circumstances under which such systems could exhibit large dielectric constants.

We find that CuPc and H_2Pc monomers and polymeric sheets do display a strong preference to stack in vacuum, with an equilibrium stacking distance of about 3 Å. Moreover, as the stacking distance decreases and approaches the equilibrium value, an insulator to metal transition is displayed by both CuPc and H_2Pc. Analysis of the optical dielectric function as a function of the stacking distance indicates that, close to the equilibrium stacking distance, large complex values of the dielectric function at low energies (characteristic of metallic behavior) result. On the other hand, at large values of the stacking distance, the system behaves as a "good" dielectric, with rather low values for the intrinsic dielectric constant (about 13 parallel to the plane of the molecule and about 2 normal to the plane, for both CuPc and H_2Pc). All conclusions are qualitatively similar to both CuPc and H_2Pc, indicating that Cu does not play a critical role in any of the aspects studied here.

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