

## Dielectric properties of Cu-phthalocyanine systems from first principles

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The authors present a first principles approach for investigating the dielectric properties of Cu-phthalocyanine (CuPc). The local position-dependent dielectric constant of CuPc oligomers is determined from the charge density induced by an external finite electric field. The dielectric constants of a CuPc monomer along and perpendicular to its plane are extracted from appropriately chosen periodic arrangements of CuPc oligomers. The authors obtain dielectric constant values of about 15 along the CuPc plane and about 3.4 perpendicular to the plane. © 2006 American Institute of Physics. [DOI: 10.1063/1.2339037]

Metal-phthalocyanines display high chemical stability, are amenable to various synthetic modifications, and are semiconducting,<sup>1</sup> due to which they have been considered for various technological applications, including thin film flexible transistors<sup>2,3</sup> and light emitting diodes.<sup>4,5</sup> Recently, copper-phthalocyanine (CuPc) oligomers have been used as a filler to a polymer matrix to develop an all organic high dielectric constant composite.<sup>6</sup> 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.<sup>7</sup>

Our recent study has established an initial understanding of the dielectric properties of Pc based monomer molecules.<sup>8</sup> The optical and static polarizability tensors of metal (Cu, Mg) Pc and metal-free (H<sub>2</sub>) Pc monomer molecules were computed using first principles density functional theory (DFT) based methods. A classical electrostatic model which approximates the planar CuPc molecule as a prolate ellipsoid was then used to estimate its dielectric tensor from the computed polarizability tensor. However, owing to the difficulty in defining the geometric attributes of the CuPc molecule, a rather broad range of dielectric constants (3–∞) was obtained along the direction perpendicular to the plane of the molecule.<sup>8</sup> Dielectric constants in the 10–20 range are expected along the plane of the molecule, based on this classical model.<sup>8</sup>

In the present contribution, the dielectric constants of CuPc monomers are determined using a fully first principles computational approach, via the theory of the local dielectric permittivity developed recently.<sup>9,10</sup> This approach requires the usage of supercell techniques, in which the effective CuPc monomer properties are extracted from appropriately chosen periodic arrangements (i.e., polymeric or oligomeric forms) of CuPc, as described below.

All calculations presented here were performed using the local density approximation within DFT (Ref. 11) as implemented in the local orbital SIESTA code.<sup>12</sup> Norm-conserving nonlocal pseudopotentials of the Troullier-Martins type were used to describe all the elements. Atomic configurations of [He]2s<sup>2</sup>2p<sup>2</sup>, [He]2s<sup>2</sup>2p<sup>3</sup>, [He]2s<sup>2</sup>2p<sup>4</sup>, and [Ar]3d<sup>10</sup>4s<sup>1</sup> were used for the C, N, O, and Cu pseudopotentials, respectively.

A double-zeta plus polarization basis set with orbital-confining cutoff radii determined by a PAO.EnergyShift parameter of 0.0001 Ry was used for all calculations.

The atomic coordinates of the CuPc monomer was optimized in the absence of an external electric field, with the requirement that the force on each atom be smaller than ±0.04 eV/Å. The CuPc monomer exists as a planar molecule, with several aromatic and nitrogen containing rings surrounding a central Cu atom. Our computed CuPc structure presented elsewhere<sup>8</sup> is in excellent agreement with prior computational work<sup>13,14</sup> and with experiments.<sup>15</sup>

*Dielectric constant along CuPc plane (ε<sup>||</sup>).* Figure 1 shows the supercell used for the computation of the polarization and dielectric constant along the plane of a CuPc monomer (i.e., along the z direction). Note that the supercell contains two CuPc *mer* units. The supercell, when replicated in three dimensions, results in a periodic array of CuPc “ribbons” with the long and short ribbon axes along the x and z directions, respectively. A vacuum region (of thickness *D*) separates a ribbon from its periodic images along the y direction. The reason two monomer units are chosen within the supercell (as opposed to just one) is to allow for an unambiguous definition of the physical extent of the equivalent of a single monomer; the region between the two Cu atoms represents a single monomer. This definition will be useful when extracting dielectric properties from the following calculations.

The geometry of the entire ribbon was optimized, followed by the application of an electric field of strength ±δ (with δ=0.01 V/Å) along the z axis.<sup>16</sup> The atomic positions

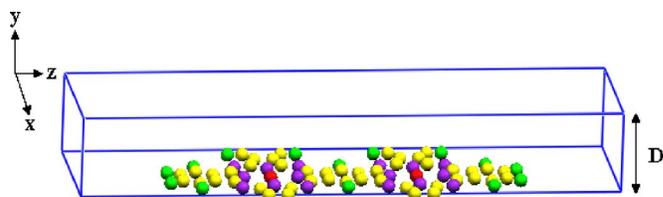


FIG. 1. (Color online) CuPc supercell used to compute the dielectric constant along the z direction. Cu atom is in red, N in purple, C in yellow, and H in green. The supercell repeats in three dimensions, resulting in an array of CuPc ribbons with their long and short axes along the x and z directions, respectively. The ribbons are two CuPc *mer* units wide and are separated by distance *D* along the y direction. A detailed description of the CuPc structure can be found in Ref. 8.

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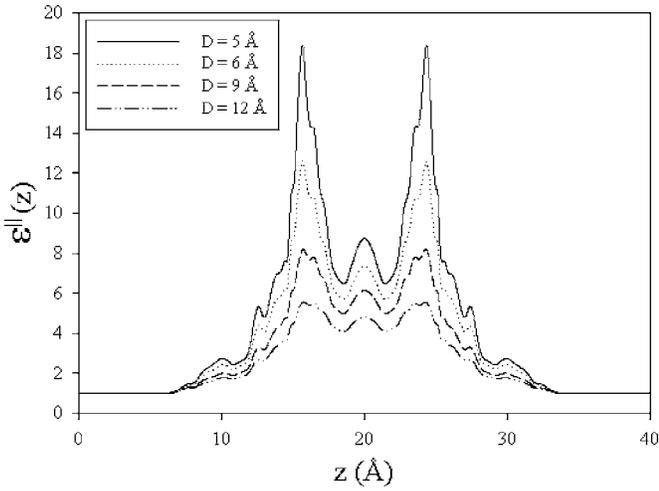


FIG. 2. Dielectric constant along the CuPc plane of a CuPc-vacuum composite for the geometry shown in Fig. 1.

were fixed at the field-free positions, while the electronic degrees of freedom were allowed to relax in response to the applied field. This implies that only the electronic contribution to the polarization and dielectric constant was addressed here. This decision was motivated by the fact that our prior work has clearly indicated that over 99% of the polarizability of CuPc is electronic in origin.<sup>8</sup>

For the supercell of Fig. 1, the local position-dependent polarization induced due to an external field along the  $z$  direction is given by<sup>17</sup>

$$\frac{d}{dz}\bar{p}(z) = -\bar{\rho}_{\text{ind}}(z), \quad (1)$$

where the  $\bar{p}(z)$  and  $\bar{\rho}_{\text{ind}}(z)$  are the polarization along the  $z$ -axis and induced charge density, respectively, averaged on the  $x$ - $y$  plane. The induced charge density  $\bar{\rho}_{\text{ind}}(z)$  was evaluated as the difference of the charge densities due to positive ( $+\delta$ ) and negative ( $-\delta$ ) external electric fields. The solution of Eq. (1), with the appropriate boundary condition (zero polarization in the middle of the vacuum regions of the supercell), provides the planar averaged position-dependent polarization, from which the position-dependent local dielectric constant profile (for linear systems, such as the ones considered here) can be determined as

$$\epsilon^{\parallel}(z) = \frac{\epsilon_0 E_{\text{ext}}}{\epsilon_0 E_{\text{ext}} - \bar{p}(z)}. \quad (2)$$

In the present work,  $E_{\text{ext}} = 2\delta = 0.02 \text{ V/\AA}$ , as  $\bar{p}(z)$  was determined from charge densities due to fields of  $+\delta$  and  $-\delta$  along the  $z$  direction separately.

Figure 2 shows the local position-dependent dielectric constant along the  $z$  axis as defined in Fig. 1, for  $D$  in the 5–12 Å range. Note that as the computed  $z$ -dependent dielectric constant profiles are a result of planar averages along the  $x$ - $y$  plane, they are a function of the parameter  $D$ . The locations of the highest two peaks in each case correspond to the location of the two Cu atoms within the supercell. As a result, the average value of the dielectric constant between the two peaks is the value corresponding to a single CuPc monomer, plus the vacuum region separating the CuPc rib-

TABLE I.  $\epsilon_{\text{CuPc comp}}^{\parallel}$  as a function of vacuum thickness  $D$ .

$D$ (Å)	$\epsilon_{\text{CuPc comp}}^{\parallel}$
5	10.48
6	8.54
9	6.16
12	4.78

bons along the  $z$  direction. These CuPc-vacuum “composite” values,  $\epsilon_{\text{CuPc comp}}^{\parallel}$ , are reported in Table I for all values of  $D$  studied.

Needless to say,  $\epsilon_{\text{CuPc comp}}^{\parallel}$  decreases with  $D$ . We can further extract the dielectric constant of an isolated CuPc molecule itself from these results using standard electromagnetic mixing theorems.<sup>18</sup> For a composite system comprising two alternately stacked dielectrics, the composite dielectric constant along a direction *normal* to the stacking direction is given by the “parallel” combination of the component “capacitors.” In this case, the component dielectric constants add up linearly in proportion to their volume fractions, resulting in

$$\epsilon_{\text{CuPc comp}}^{\parallel} = \epsilon_{\text{CuPc}}^{\parallel} d_{\text{CuPc}}/D + \epsilon_{\text{vac}} d_{\text{vac}}/D, \quad (3)$$

where  $d_{\text{CuPc}}$  and  $d_{\text{vac}}$  are the thicknesses of the CuPc and vacuum regions, respectively, along the  $y$  direction (with  $d_{\text{CuPc}} + d_{\text{vac}} = D$ ), and  $\epsilon_{\text{CuPc}}^{\parallel}$  and  $\epsilon_{\text{vac}}$  are their respective dielectric constants normal to the stacking direction. In our composite system,  $\epsilon_{\text{vac}} = 1$ , and Eq. (3) reduces to

$$\epsilon_{\text{CuPc comp}}^{\parallel} = (\epsilon_{\text{CuPc}}^{\parallel} - 1)d_{\text{CuPc}}/D + 1. \quad (4)$$

Figure 3 shows a plot of the computed  $\epsilon_{\text{CuPc comp}}^{\parallel}$  values (Table I) versus  $1/D$ . Indeed, a linear relationship between these two quantities with an intercept of 1 was obtained, as required by the above equation. If we make the further assumption that  $d_{\text{CuPc}} \approx 3 \text{ Å}$ ,<sup>19</sup> the slope of the linear fit of Fig. 3 (given as  $(\epsilon_{\text{CuPc}}^{\parallel} - 1)d_{\text{CuPc}}$ ) yields the dielectric constant of CuPc molecule along its plane as  $\approx 15$ , consistent with our prior semiclassical estimate of 10–20.<sup>8</sup>

*Dielectric constant perpendicular to CuPc plane ( $\epsilon^{\perp}$ ).*

For this case, the supercell consisted of a single monomer unit with its plane normal along the  $z$  axis, such that when

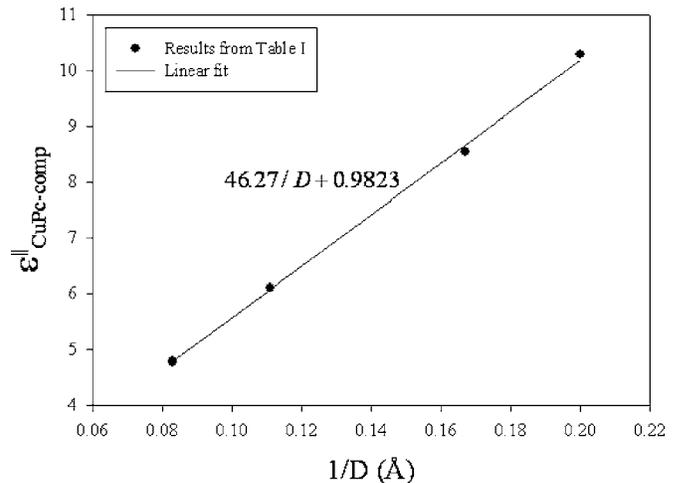


FIG. 3.  $\epsilon_{\text{CuPc comp}}^{\parallel}$  along the CuPc plane as a function of  $1/D$ . A fit to the functional form of Eq. (4) is also shown.

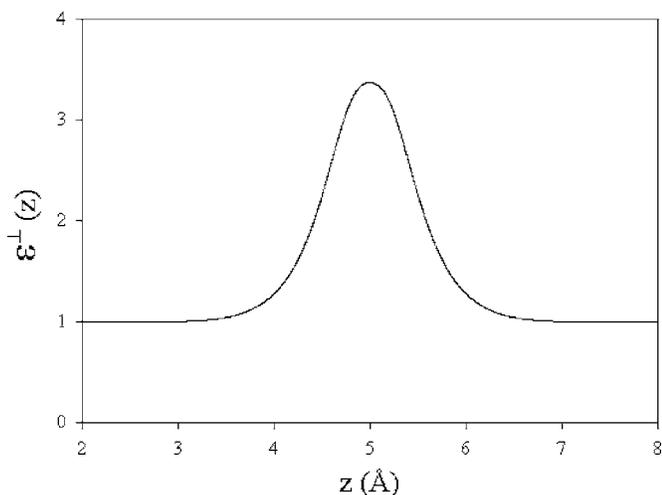


FIG. 4. Dielectric constant of the equivalent of a CuPc monomer as a function of position  $z$  normal to the CuPc plane. The CuPc plane is located at  $z=5$  Å.

repeated in three dimensions, an array of CuPc sheets would result (while a single isolated monomer would have H atoms passivating the outermost atoms, here, the H atoms are absent to allow for bonding between adjacent *mer* units). The  $z$  dimension of the supercell was chosen large enough ( $>40$  Å) so that interaction between two adjacent CuPc sheets is negligible. The  $z$ -dependent polarization and dielectric constant along the  $z$  direction were determined using the procedure described above [Eqs. (1) and (2)]. In this case, planar averaging along the  $xy$  plane implies an average over the equivalent of one CuPc *mer* unit. Figure 4 shows the computed dielectric constant as a function of position normal to the CuPc plane, with the CuPc plane located at  $z=5$  Å. It can be seen that the maximum value of the dielectric constant is  $\approx 3.4$ , consistent with the lower end of the wide range of values ( $3-\infty$ ) predicted by our prior semiclassical model.<sup>8</sup>

In summary, we have presented a first principles approach for investigating the dielectric properties of CuPc, using the theory of the local dielectric permittivity. The dielectric constant of a single CuPc *mer* unit along and perpendicular to its plane are extracted from appropriately chosen periodic arrangements of CuPc. We obtain dielectric constant

values of about 15 along the CuPc plane and about 3.4 perpendicular to the plane. These results indicate that CuPc monomers do not intrinsically have a high dielectric constant. Other factors (such as oligomerization, stacking, contact electrodes, etc.) could result in the observed high dielectric constant values of CuPc systems and are currently under investigation.

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- <sup>1</sup>D. D. Eley, *Nature (London)* **162**, 819 (1948).
- <sup>2</sup>P. R. L. Malenfant, C. D. Dimitrakopoulos, J. D. Gelorme, L. L. Kosbar, T. O. Graham, A. Curioni, and W. Andreoni, *Appl. Phys. Lett.* **80**, 2517 (2002).
- <sup>3</sup>C. Rost, D. J. Gundlach, S. Karg, and W. Riess, *J. Appl. Phys.* **95**, 5782 (2004).
- <sup>4</sup>C. Ego, D. Marsitzky, S. Becker, J. Zhang, A. C. Grimsdale, K. Müllen, J. D. Mackenzie, C. Silva, and R. H. Friend, *J. Am. Chem. Soc.* **125**, 437 (2003).
- <sup>5</sup>I. Seguy, P. Jolinat, P. Destruel, J. Farenc, R. Mamy, H. Bock, J. Ip, and T. P. J. Nguyen, *J. Appl. Phys.* **89**, 5442 (2001).
- <sup>6</sup>Q. M. Zhang, H. Li, M. Poh, F. Xia, Z.-Y. Cheng, H. Xu, and C. Huang, *Nature (London)* **419**, 284 (2002).
- <sup>7</sup>T. Kreouzis, K. J. Donoban, R. J. Bushby, O. R. Lozman, and Q. Liu, *J. Chem. Phys.* **114**, 1797 (2001).
- <sup>8</sup>R. Ramprasad and N. Shi, *Appl. Phys. Lett.* **88**, 222903 (2006).
- <sup>9</sup>F. Giustino and A. Pasquarello, *Phys. Rev. B* **71**, 144104 (2005).
- <sup>10</sup>N. Shi and R. Ramprasad, *Phys. Rev. B* **74**, 045318 (2006).
- <sup>11</sup>R. Martin, *Electronic Structure: Basic Theory and Practical Methods* (Cambridge University Press, New York, 2004).
- <sup>12</sup>J. M. Soler, E. Artacho, J. Gale, A. Garcia, J. Junquera, P. Ordejon, and D. Sanchez-Portal, *J. Phys.: Condens. Matter* **14**, 2745 (2002).
- <sup>13</sup>X. Zhang, Y. Zhang, and J. Jiang, *J. Mol. Struct.: THEOCHEM* **673**, 103 (2004).
- <sup>14</sup>D. Li, Z. Peng, L. Deng, Y. Shen, and Y. Zhou, *Vib. Spectrosc.* **39**, 191 (2005).
- <sup>15</sup>C. J. Brown, *J. Chem. Soc. A* **1968**, 2488.
- <sup>16</sup>External electric field along the  $\pm z$  directions are applied purely due to numerical reasons and is most applicable for asymmetric situations. In the present case, since the system is symmetric along the  $\pm z$  directions, the induced charge density along the  $+z$  direction can be obtained from that along the  $-z$  direction purely from symmetry.
- <sup>17</sup>J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1998).
- <sup>18</sup>Ari Sihvola, *Electromagnetic Mixing Formulas and Applications* (The Institution of Electrical Engineers, London, UK, 1999).
- <sup>19</sup>This choice of  $d_{\text{CuPc}}$  was motivated by the fact that CuPc oligomers tend to stack with interplanar distance of about 3 Å, indicating that this distance can be viewed as the effective thickness of a CuPc layer.