



Gas sensing behavior of metal-phthalocyanines: Effects of electronic structure on sensitivity



Malay Kumar Rana^a, Mousumi Sinha^{a,b}, Siddhartha Panda^{a,b,*}

^a National Centre for Flexible Electronics, Indian Institute of Technology Kanpur, Kanpur 208016, India

^b Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India

ARTICLE INFO

Keywords:

Chemical sensing
VOC
Phthalocyanine
DFT
Binding energy
Mulliken electronegativity

ABSTRACT

Cu-phthalocyanine (CuPc) and five of its metal variants (M = Mg, Mn, Co, Ni, and Zn) have been studied by density functional theory (DFT) methods for sensing five volatile organic compounds – isoprene, acetone, ammonia, methanol, and methane. Having performed experimental validation of the methods, interaction energies, binding configurations, changes in charge distributions and energy levels after interaction, and interaction barriers were studied to account for the sensitivity trend across the analytes for CuPc, while also providing [supporting data](#) from experiments carried out herein. It is also demonstrated that relatively simple calculations of interaction barrier can result in quick screening of metal-Pc variants for an analyte without any extensive experimental or computational efforts. Present literature lacks such detailed studies for these materials and analytes. Thus, this work would consolidate the understanding of sensing phenomena at the electronic structure level that could be useful for emerging technologies in gas sensing.

1. Introduction

Since their discovery [1–4], phthalocyanine (Pc) compounds have been widely being utilized as catalysts and in advanced technological fields such as solar cells, optics and semiconductors [5–9]. Their special properties are attributed to the molecular level features offered by highly delocalized π electrons in metal embedded Pcs. Different Pc molecules have also been used as gas sensing materials. Sensing of NO₂ [10–18], Cl₂ [19–22], CO₂ [23,24], NH₃ [25,26], and some volatile organic compounds (VOCs) [27,28], e.g., benzene, toluene, ethanol, and methanol has been performed by MPc (M = H₂, Cu, Co, Pb, Zn, Fe, Pd) or their functionalized derivatives using thin films, nanocolumns [29] or nanobelts [30] as the platform. CuPc has been a prototype material in most cases [11,13,14,20,21,29]. Sensitivity studies are primarily based on monitoring the conductance variation of the materials after exposure to an analyte, although spectroscopic/chemiluminescence techniques have also been used in some cases [31]. Bohrer et al. demonstrated the sensitivity trend across a group of electron rich analytes (twelve) and correlated to their basicity [32]. Radhakrishnan et al. emphasized that the sensitivity of polymeric materials (e.g., polyaniline, polypyrrole and polythiophene) can be enhanced by functionalization with CuPc due to its strong interaction with the analytes [33]. These studies indicate the potential of MPc molecules for sensing applications and thus a detailed understanding of the sensing

mechanisms is essential for rapid selection of promising Pc materials for sensing different gases. While the information at the electronic structure level can be very helpful to understand the sensing phenomena and the mechanisms, lack of such information or fewer specific studies (described below) limit the effective utilization of these molecules.

Density functional theory (DFT) [34–36] has been found to be a useful tool for predicting the electronic structure properties of various MPcs (M = Cu, Ni, Zn, and Mg) [37–44]. Within DFT, various semi-local and hybrid functionals were benchmarked to reproduce the experimental photoemission data of CuPc [40]; the Heyd–Scuseria–Ernzerhof (HSE) screened hybrid functional [45] was found to be more accurate slightly at higher computational costs than semi-local functionals. However, the major attention has been directed towards describing the electrocatalytic role of MPcs (M = Fe, Cr, Co, Ni) with DFT through the study of oxidation-reduction reactions. There is limited adoption of DFT specifically in gas sensing with MPcs. Parkhomenko et al. used DFT to explain the higher sensitivity of PdPcF₁₆ compared to unsubstituted PdPc towards NH₃ and H₂ [46]. They computed only the binding geometries, binding energies and atomic partial charges. The higher sensitivity of fluorinated compound was justified by lower binding energy and greater degree of charge transfer with the analytes. A similar analysis was done by Klyamer et al. for NH₃ sensing with CoPc and CoPcF₄ [47]. Again from the computation of binding energies, Tran et al. [48] demonstrated successfully the trend of

* Corresponding author at: National Centre for Flexible Electronics, Indian Institute of Technology Kanpur, Kanpur 208016, India.
E-mail address: spanda@iitk.ac.in (S. Panda).

basicity and sensitivity of ZnPc for twelve electron rich analytes such as dichloromethane, nitromethane, trimethylphosphate, isophorone, dimethylsulfoxide, etc. in accordance with the experiments reported earlier by Bohrer et al. [32]. Apart from these specific studies on gas sensing, no further efforts have been attempted to predict in advance and understand the sensing behavior of MPcs for other gases or VOCs with DFT. The present work has, in comparison to the previous studies, addressed wider scope – six MPcs (M = Cu, Mg, Mn, Co, Ni, and Zn) and five analytes (isoprene, acetone, ammonia, methanol, and methane) of different molecular characteristics, carried out a detailed study beyond the binding energy and partial charge analysis such as characteristics of charge density differences, molecular energy levels, interaction barriers, and absorption spectra. DFT methods are benchmarked here with experimental data and improved exchange energy functionals with dispersion flavor are used to ensure better accuracy. The binding mode of analytes to MPc is described in detail by various geometrical parameters (bond lengths, angles, dihedrals, etc.).

As CuPc is an important molecule for gas sensing [10–14, 19,25,32,33], it has been chosen to predict its relative response towards five different VOC molecules, namely- (i) isoprene, (ii) acetone, (iii) ammonia, (iv) methanol, and (v) methane. So as to reinforce the prediction capability or understandings gained from the study with CuPc, five other MPcs (M = Mg, Mn, Co, Ni, and Zn) were tested further for an analyte. The gases are chosen to take into account the diverse features of analytes such as having π electrons, lone pairs, both (π and lone pair electrons) or none of these. In addition, they are reported to be indicators of several diseases [49–55]. An advanced version of DFT with dispersion correction, Grimme's D2 method, was used [56]. The binding energy of CuPc for each analyte molecule was calculated from which the sensitivity trend was established. The reasons behind the sensitivity trend across the analytes were further investigated at the electronic level by computing atomic partial charges, charge density differences, molecular orbitals (MO), band gaps, Mulliken electronegativities and UV–Vis spectra. Along with the optimized geometries, the atomic partial charges and charge density difference plots provide valuable insights into the interaction mechanism of CuPc with the analytes. As mentioned, in addition to the simulation techniques used here, a set of different experiments were performed to support the observations from the simulated results. Learning from this study could be utilized in selecting and designing molecules for gas sensing; and specifically in the emerging field of breath analysis for early disease detection [57–61].

2. Materials and methods

2.1. Computational details

The sensing ability of CuPc towards five different analyte molecules- (i) isoprene, (ii) acetone, (iii) ammonia, (iv) methanol, and (v) methane were studied with the Gaussian 09 program. The density functional theory (DFT) [34] calculations employing Grimme's dispersion corrected D2 method were performed using the GGA B97D and the hybrid meta-GGA WB97XD functionals [56]. The widely used 6-31g(d) basis set was adopted for all atoms. In addition, a combination of LANL2DZ basis set for Cu and 6-31g(d) basis set for rest of the atoms was used with the B97D functional. Unlike the 6-31g(d) basis set, the LANL2DZ is provided with an effective core potential (ecp) for transition metals, which reduces the computational cost. Thus, calculations were performed with three different methods, namely – (i) Method 1: B97D/6-31g(d), (ii) Method 2: WB97XD/6-31g(d), and (iii) Method 3: B97D/6-31g(d) + LANL2DZ (Cu). Geometry optimization was carried out within the default convergence criteria (Max Force = 0.00045, RMS Force = 0.0003, Max Displacement = 0.0018 and RMS Displacement = 0.0012) for CuPc, analytes, and the CuPc-analyte complexes by each method. The binding energy (BE) was then computed for each analyte as $BE = E_{\text{CuPc-analyte}} - E_{\text{CuPc}} - E_{\text{analyte}}$, where E corresponds to

the energy of the optimized geometry. Counterpoise correction (CP) to BE was made such that the CP corrected energies are $BE^{\text{CP}} = BE + BSSE$ to remove the basis set superposition error (BSSE) arising due to the use of finite basis sets.

Computations of optimized geometrical parameters (distances between atoms, bond angles, dihedral angles, etc.) for CuPc, analytes, and the CuPc-analyte complexes, atomic partial charges from fitting of the electrostatic surface potential (ESP), energies for the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), the band gap, and the Mulliken electronegativity (E_{η}) were performed. $E_{\eta} = 0.5 (EA - IP)$, where EA and IP are electron affinity and ionization potential, respectively. Within the tight convergence of the self-consistent field (SCF), the charge density difference was determined for each complex. UV–Vis spectra were simulated in chloroform solvent by time-dependent density functional (TD-DFT) employing the above-mentioned methods. The geometries of another five metal embedded Pcs, MPc (M = Mg, Mn, Co, Ni, and Zn) were optimized with Method 2 and BE was calculated for isoprene. For MPc and MPc-analyte complexes, unrestricted formalism has been employed in the calculations. The calculations are performed using the unrestricted formalism for systems having odd number of electrons, such as Mn, Co, CuPc, and their complexes with the analytes, and this excludes Ni, Zn, and MgPc or their complexes with the analytes. The calculations correspond to C1 symmetry both for MPcs and their analyte complexes. The MPcs and their analyte complexes with M = Co and Cu correspond to the spin state $S = 1/2$, M = Mn corresponds to $S = 5/2$, while the rest including the analytes correspond to the spin state $S = 0$. These magnetic states of the MPcs or their complexes are in accordance with the previous electronic structure calculations [62,63]. In the previous electronic structure calculations, the interaction energy computed for the analytes with MPcs account for the overall effect of both α and β spins.

2.2. Experimental details

Single crystal X-ray crystallography data were taken for CuPc (Bruker Smart Apex Single Crystal – XRD). 1 M solution of CuPc in tetrahydrofuran (THF) solvent was prepared from which 1% analyte solution was prepared by adding 1 ml of an analyte to 99 ml of CuPc-THF solution. The solvent, tetrahydrofuran (THF) received from Sigma Aldrich was analytical grade, anhydrous, assay $\geq 99.9\%$, inhibitor-free, and was used as is without any further purification. UV–vis spectra were obtained from a spectrophotometer (Cary Varian 5000 UV Spectroscopy) using a scan speed of 120 nm/min with data interval of 1 nm in the range 250–850 nm, and a slit width of 2 nm. Cyclic voltammograms were obtained using an electrochemical workstation (Autolab, Metrohm) with an Ag/AgCl reference electrode. With the oxidation and reduction potentials obtained therein, HOMO and LUMO for CuPc-analyte complexes can be computed as: $HOMO = -[E_{\text{ox}} + 4.4] \text{ eV}$ and $LUMO = -[E_{\text{red}} + 4.4] \text{ eV}$. E_{ox} and E_{red} are, respectively, oxidation and reduction potentials with 4.4 eV being the potential of the reference electrode, Ag/AgCl [64].

3. Results and discussion

In Section 3.1, the DFT optimized CuPc structures are compared with structures obtained from the single crystal X-ray crystallography experiments performed in this work and the available literature data to validate the computational methods. In Section 3.2, the energetics of interaction of the analytes with CuPc are discussed and the corresponding binding geometries are described in Section 3.3. In Section 3.4, the atomic partial charge distributions in the CuPc-analyte complexes relative to the constituent molecules are compared and related to the trend of interaction energies across the analytes, whereas in Section 3.5, the charge density differences in the complexes are illustrated. A description of the molecular energy levels in CuPc, the analytes and their complexes is provided along with the experimental cyclic

Download English Version:

<https://daneshyari.com/en/article/7837067>

Download Persian Version:

<https://daneshyari.com/article/7837067>

[Daneshyari.com](https://daneshyari.com)