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Experimental and density functional theory study on humidity sensing properties of copper phthalocyanine (CuPc)

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Abstract

The quartz crystal microbalance (QCM) technique was applied to investigate humidity sensing properties of a copper phthalocyanine (CuPc) thin film prepared by drop cast method. The humidity adsorption and desorption kinetics of (CuPc) thin film was evaluated. The QCM and electrical measurements results showed that humidity sensing properties of CuPc is very sensitive to humidity changes and reversible adsorption/desorption performance which is an indicative of a good humidity sensor even at room temperature. Reproducible experimental results indicated that CuPc thin films have an abundant potential for humidity sensing applications at ambient temperature. According to the first-principle density functional theory calculations, the promising humidity sensing properties of CuPc can be attributed to the considerable charge transfer from the water molecule into Cu atom.

Keywords: Copper Phthalocyanine (CuPc), Humidity sensor, Thin film, Quartz crystal microbalance, DFT calculations.

1. Introduction

Controlling and monitoring of environment parameters such as gases in the air, suspended particles, humidity and etc. are a significant issue for evaluation of environmental conditions and utilization of industrial facilities [1–3]. The humidity is one of the main issues in many industries like oil and agriculture. Consequently, preparing reliable, inexpensive, and highly sensitive humidity sensors to detect water molecules remains as an important and challenging research issue. During the last decade, many types of materials based on ceramic, carbon based materials, polymeric materials have been introduced as humidity sensors [4–6]. Recently, semiconductors and organic materials have been used as practical humidity sensors [7,8]. Among them, devices based on organic semiconducting materials due to their low cost, easy fabrication, exciting electrical and optical properties have attracted huge attention. Also, some organic semiconductors have been applied in commercially produced light emitting diodes (LEDs). Some are very sensitive to humidity temperature, IR, visible and UV radiation, and even to different types of gases such as ammonia. Accordingly, evaluating of organic semiconductors properties such as physical characteristics under diverse situations is a very capable field for improvement of humidity sensors, light radiation, temperature, strain, gases, etc [9–11]. Indeed, organic semiconductors will catch more positions amongst the electronic materials in the close future.

Transition-metals phthalocyanines are considered as a special class of organic molecules with wide-ranging applications. Copper phthalocyanine (CuPc) films, in particular, are used in such diverse applications as organic light emitting diodes (OLEDs)[11], solar cells [12], dyes [13], field-effect transistors [14], and surface conductivity-based gas sensors [15,16]. Moreover, the humidity adsorption and desorption studies of CuPc are very important for many humidity and gas sensing device applications [17–20]. The molecular structure of CuPc is shown in Fig.1.

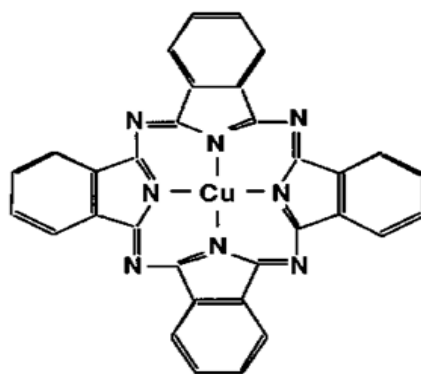


Fig.1 The molecular structure of CuPc.

Quartz crystal microbalance (QCM) is a technique widely used to evaluate the resonant frequency changes. This resonant frequency is sensitive to mass change of the crystal. The mass change (Δm) from the measured frequency change (Δf) is obtained by using the Saurbey equation [20]:

$$\Delta f = -\frac{2f_0^2 \Delta m}{A\sqrt{\mu\rho}} \quad (1)$$

in which f_0 is the resonant frequency of the QCM crystal, ρ is the density of the crystal, μ is the shear modulus of quartz and A is the area of the gold disk on the crystal.

2. Experiment

CuPc films of various thicknesses were prepared according to the following procedure. Commercially purchased CuPc powders from Sigma-Aldrich. CuPc molecules (99% Purity) were solved in toluene with 1 mg/ml concentration and 5 μ l of solution were coated onto surface of QCM by drop-casting method. After evaporation of toluene, thicknesses of CuPc film was measured as 300nm with Dektak 150 profilometer of Veeco. For the electrical characterizations, Au metal with high purity (99.9%) was thermally evaporated on the CuPc film. In the field of humidity sensors implementing sensitive materials, the structure and morphology of thin films are very important characteristics. Thus, to correlate sensing properties with thin films, OM micrograph of CuPc film in different magnifications was shown in Fig. 2. As seen, the morphology of the prepared films consist columnar and fiber like structure. These types' structures gave high surface area that are suitable for sensor application.

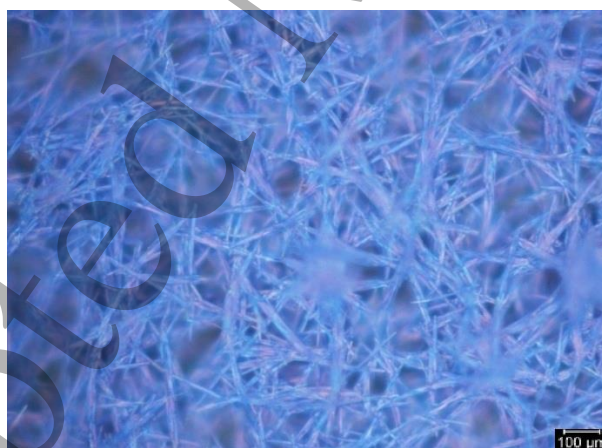
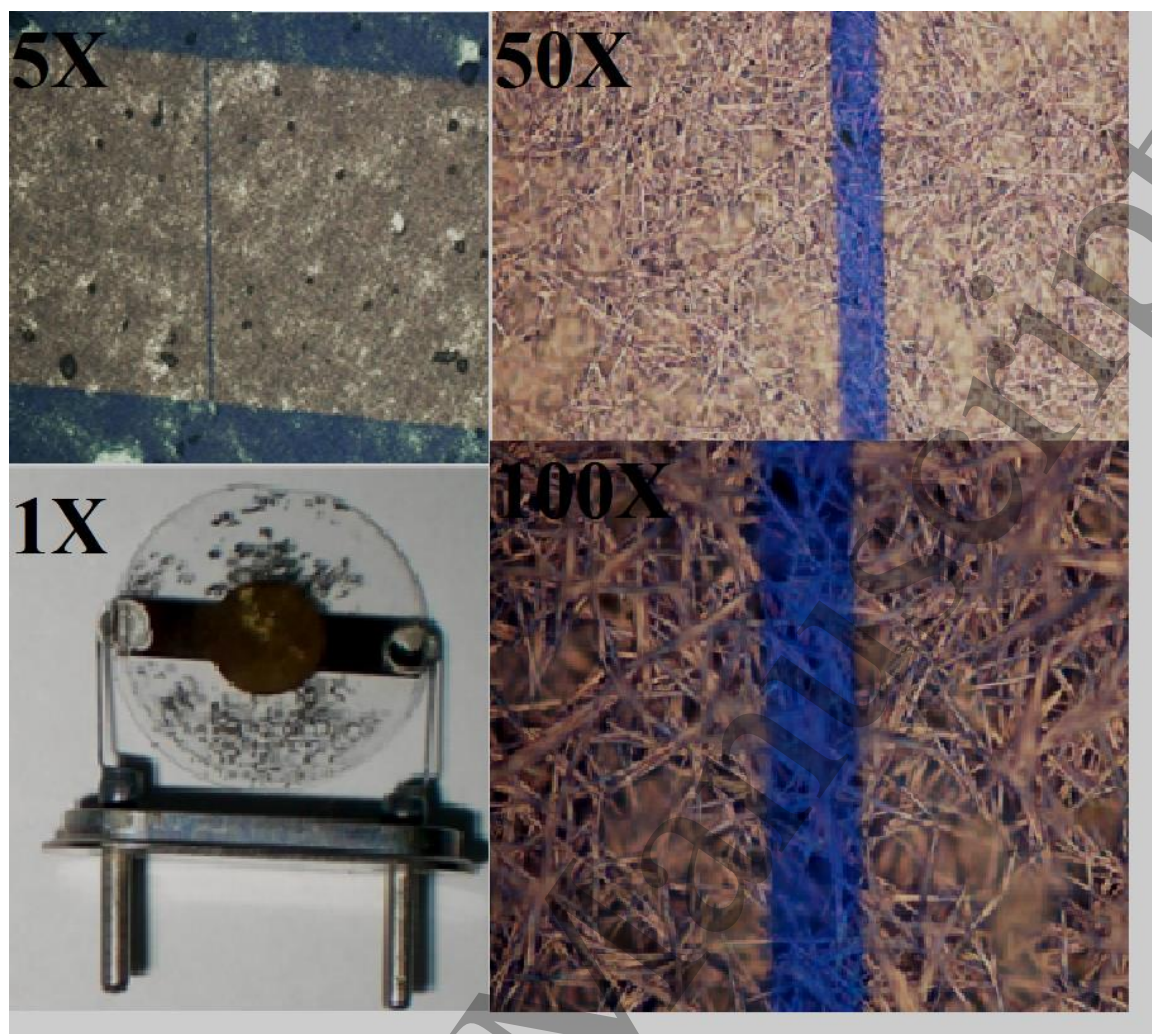


Fig. 2. OM micrograph of CuPc film in different magnifications.

In our study, we used QCM with the model of CHI400A Series from CH, after exposure of the crystal mass loading of water molecules at different humidity environments e.g. at 11%, 22%, 43%, 55%, 75%, 84%, 94%, 97% relative humidity (RH) in a closed box partly filled with saturated salt solutions generates relative humidity in the free room above the salt with good accuracy. The value of the relative humidity depends on the type of salt

used in Table 1. The concentration that was mentioned in table 1 is the calculated vapor molar concentration C using ideal gas equation ($PV = nRT$) at the corresponding partial pressure for the relative humidity measured at the equilibrium point c . For saturated LiCl, the humidity was fixed at 11% RH and for K_2SO_4 at 97% RH) aquatic solution level inside a half-filled closed container using hybrid system of QCM electrodes and a commercial humidity/temperature EI-1050 sensor with a single chip module (SHT11) manufactured by Sensirion (Staefa, Switzerland). Both signals coming from QCM and RH sensor were simultaneously measured during the adsorption process. Both the relative humidity and temperature were also recorded during measurements to maintain the temperature at 20C.

Table 1. The relative humidity (RH) conditions (from reference [20])

Saturated solutions	Relative humidity (%)	Concentration (M)
LiCl	11	1.06E-04
KAc	22	2.11E-04
K_2O_3	43	4.13E-04
$Mg(NO_3)_2$	55	5.28E-04
NaCl	75	7.20E-04
Ka	84	8.06E-04
KNO_3	94	8.37E-04
K_2SO_4	97	9.31E-04

To describe the adsorption and desorption kinetics of gas vapor molecules onto organic or inorganic films, the Langmuir adsorption isotherm model was employed:

$$\frac{d\theta}{dt} = k_a(1-\theta)C - k_d\theta \quad (2)$$

where θ is the fraction of surface coverage; C is the humidity concentration; k_a is the rate constant for the adsorption and k_d is the rate constant for the desorption.

Integration of Eq. (2) leads to:

$$\theta(t) = K'(1 - e^{-k_{obs}t}) \quad (3)$$

in which K' is the association constant and k_{obs} is the inverse of the relation time defined as following [20]:

$$K' = \frac{C}{C + (k_a/k_d)} \quad 5$$

$$\text{and } k_{\text{obs}} = k_a C + k_d \quad (4)$$

In the QCM technique, the frequency shift is proportional with the change in the adsorbed mass by the film on the QCM electrodes. Thus, the time variation of the change in the frequency due to adsorption can be obtained as following:

$$\Delta f(t) = \Delta f_{\text{max}} K' (1 - e^{-k_{\text{obs}} t}) \quad (5)$$

Here, the frequency shift data due to the adsorption and desorption responses against humidity changes in time intervals can be used to fit equation (6) to calculate K' and k_{obs} to obtain k_a and k_d . For our QCM sensor parameters, the manufacturer was given as $\Delta m = -(1.34 \text{ ng/Hz}) \Delta f$. Using the Sauerbrey relation given in Eq. (1), the time dependent variation of mass of the adsorbed water vapor molecules on the CuPC film surface $\Delta m(t)$ can be defined as following:

$$\Delta m(t) = \Delta m_{\text{max}} (1 - e^{-k_{\text{obs}} t}) \quad (6)$$

where Δm_{max} is the maximum adsorbed amount of the humidity molecules on the surface at $t \rightarrow \infty$ and $1/k_{\text{obs}}$ is the recovery time τ . Fig. 3 depicts the schematic setup of QCM to evaluate the adsorption and desorption kinetics.

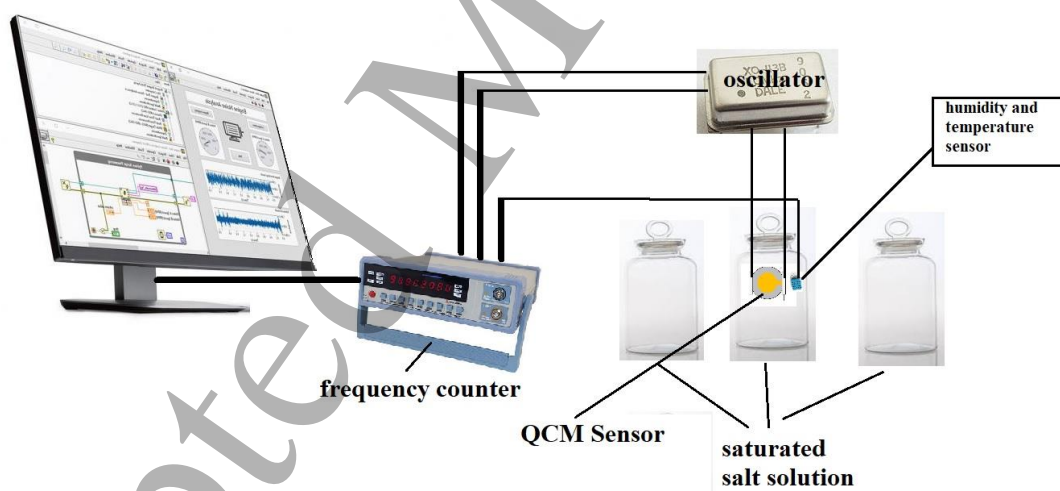


Fig. 3. The schematic setup of QCM to evaluate the adsorption and desorption kinetics of prepare sample.

3. Computational details

The spin-polarized density functional theory (DFT) calculations were performed by means of the DMol³ [22,23]. The geometry optimizations and the electronic structure calculations were carried out using the HSE screened hybrid functional [24]. The wave

function of each atom was expanded by a double-numerical basis set augmented with the polarization function (DNP). During the structural optimization, no symmetry constraints were imposed. To consider the dispersion effects, the HSE+D2 approach within the Grimme's scheme [25,26] was applied. Also, for the geometry optimization, the convergence tolerances were set to 10^{-5} Ha (1 Ha = 27.212 eV) for the energy, 0.001 Ha/Å for the force, 0.005 Å for the displacement and the basis set cut-off 4.6 Å were used.

The adsorption energy (E_{ads}) of water molecule over the CuPc substrate was obtained by the following equation:

$$E_{\text{ads}} = E_{\text{water/CuPc}} - E_{\text{CuPc}} - E_{\text{water}} \quad (7)$$

where $E_{\text{water/CuPc}}$ is the total energy of water adsorbed over the CuPc, E_{CuPc} is the energy of relaxed CuPc molecule and E_{water} is the energy of an isolated water molecule. The atomic charges and charge-transfer value were calculated by means of the Hirshfeld [27] analysis.

4. Results and discussion

Figs. 4a and b display the frequency response of CuPc coating covered QCM during the adsorption process. In Fig. 4a, after adsorption and desorption cycles between 11%, 22%, 43%, 55%, 75%, 84%, 94% and 97% RH, the QCM frequency shifts recover back to the initial value. In Fig. 4b, the CuPc sample displays a very fast adsorption and desorption response for humidity changes in short time periods to see if there is any residual adsorbed mass left on the CuPc film.

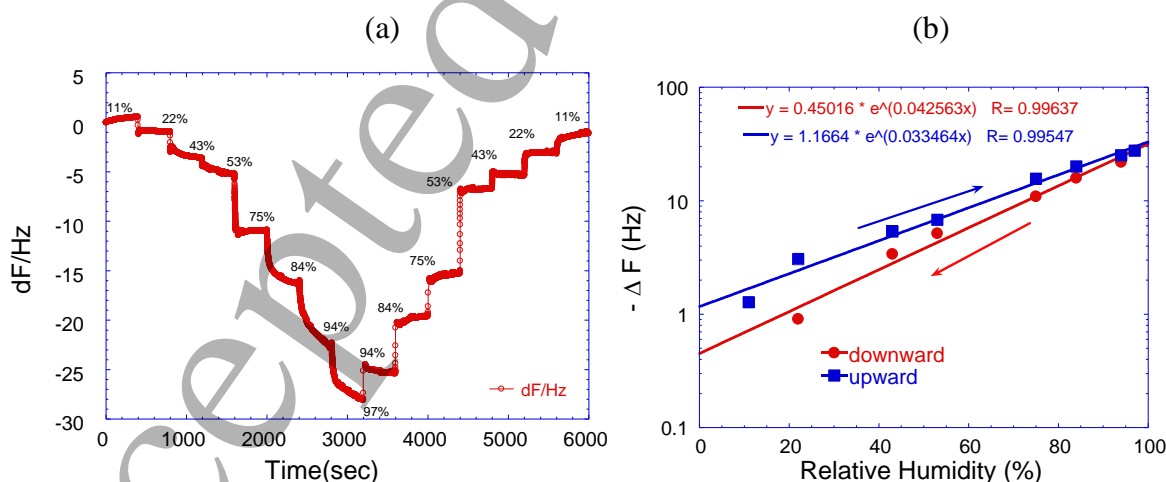


Fig.4. The frequency response of CuPc thin films covered QCM adsorption–desorption process at fixed point relative humidity conditions between 11% and 97% RH.

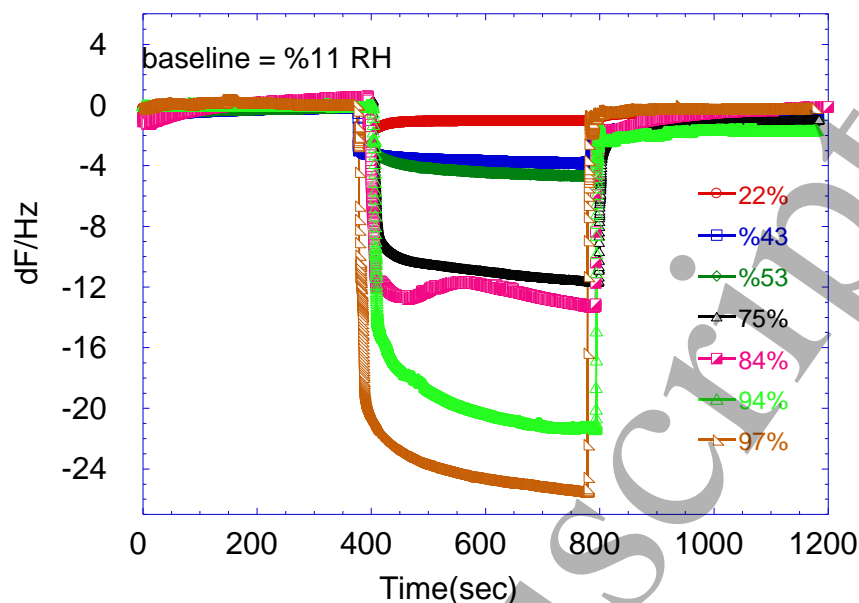


Fig. 5. Comparison of frequency shifts between 11% and 97% RH

The QCM results reveal that the CuPc layers are very sensitive to humidity and give reproducible adsorption kinetics contrary to humidity changes for short time intervals. The obtained results also indicate that the CuPc samples are reasonably steady for humidity variations during testing. The time dependent frequency shift fitted to the Langmuir isotherm adsorption (Eq. 6) is given in Fig. 6. From the curve fit, association constant (K') of the water vapor molecules is found as 44.3, and $k_{\text{obs}} = 0.139 \text{ s}^{-1}$, so the relaxation time of the adsorption process is calculated to be 7.2 s. The average values of adsorption rate k_a and k_d , are obtained as $7.36 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ and 38.14 s^{-1} , respectively. These results show that the water adsorption rates are very high in CuPC film.

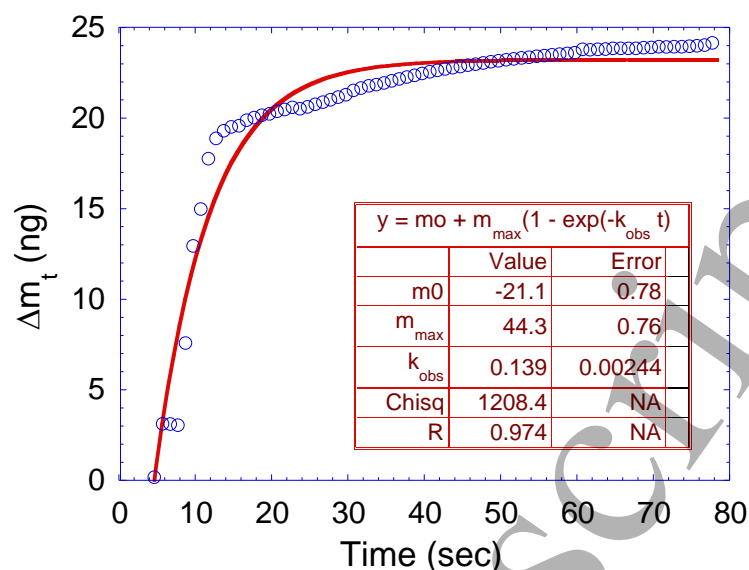


Fig. 6. The least square fit (solid line) of the adsorption part to the Langmuir adsorption isotherm model given in Eq. (6)

To get more information about the sensing mechanism of CuPc, we also performed high level DFT calculations on the possible adsorption configurations of water molecules over this substrate. Figure 7a displays the most energetically stable geometry of CuPc. As seen, the Cu atom is located between the N atoms and forms four covalent bonds with these atoms. The calculated Cu-N bond distances in the CuPc are 1.97 Å, which are in reasonable agreement with those of reported by former theoretical studies [27]. According to the Hirshfeld charge density analysis, there is a sizable charge-transfer from the Cu atom to its neighboring N atoms. As a result, the Cu atom acquires a positive charge of 0.40 e. The calculated band gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of CuPc is 1.60 eV, suggesting that it is a narrow band gap semiconductor. Meanwhile, this value is consistent with the experimental optical gap of CuPc thin films (1.70 eV) [28].

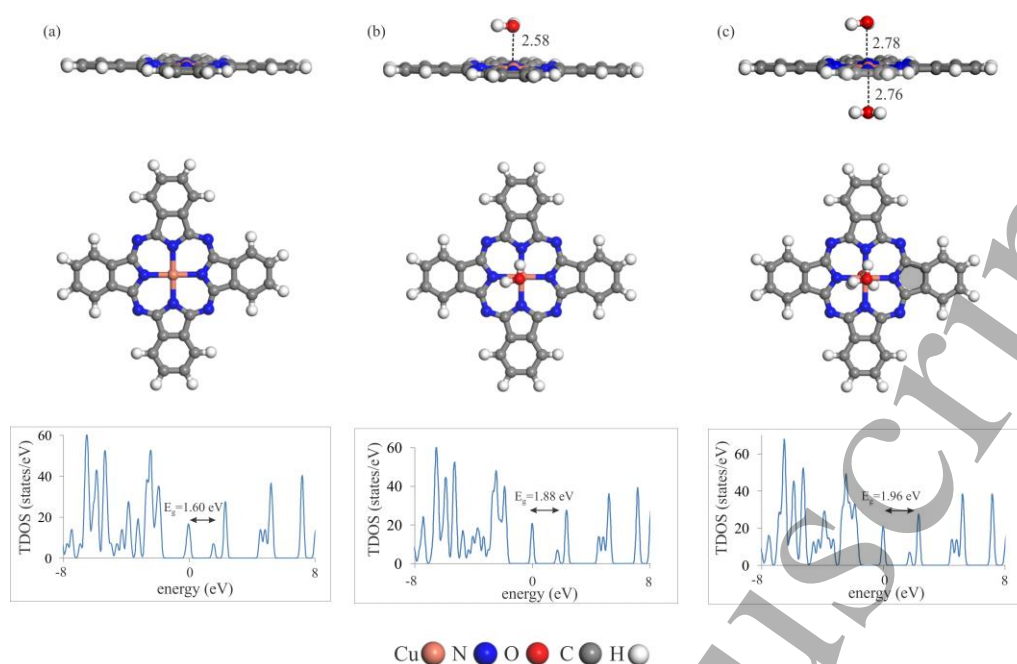


Fig. 7. The optimized structure from side (above) and top views (below), and TDOS plot of (a) CuPc, (b) CuPc/H₂O and (c) CuPc/2H₂O. In the TDOS plot, E_g corresponds to the energy gap between the HOMO and LUMO state. All bond distances are in Å.

In order to obtain the most energetically favorable site for the adsorption of the water molecules, various sites on the CuPc were examined, including the top site of the Cu atom, its neighboring N or amine nitrogen atoms. Our results indicated that the water molecules prefer to be adsorbed over the Cu atom, mainly due to the localization of a sizable positive charge density (Figures 7b and c). The binding distance between the O atom of first water molecule and Cu atom is calculated to be 2.58 Å, which is much shorter than the sum of the van der Waals radii of these atoms. Meanwhile, the adsorption energy of the H₂O is -0.26 eV, indicating that there is a fairly strong interaction between this molecule and the Cu atom. Due to the adsorption of H₂O, about 0.04 e are transferred from this molecule to CuPc. This leads to an increase in the energy of LUMO state and therefore an increase in the band gap of the CuPc. Although the addition of the second water molecule results in a weakening in the binding distance of the first water molecule, however, our results reveal that this able to further open the HOMO-LUMO gap of the CuPc. Consequently, the HOMO-LUMO gap of CuPc/2H₂O system is calculated to be 1.96 eV, which is about 23% larger than that of bare CuPc. These results, which are in excellent agreement with our experimental observations, suggest that CuPc can be viewed as an efficient and promising humidity sensing material.

5. Conclusion

Our QCM and electrical measurements results showed that humidity sensing properties of CuPc is extremely sensitive to humidity changes and reversible adsorption/desorption performance which is an indicative of a good humidity sensor even at room temperature. Thus, newly developed CuPc thin film gas sensors might be very useful as humidity sensors. According to the DFT calculations, the high sensitivity of CuPc toward the water molecules can be attributed to the considerable charge transfer from the water molecules into the Cu atom.

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