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Molecules interaction between copper phtholocyanine and volatile organic compounds with applying for gas sensor by Monte Carlo simulation

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Abstract

The molecular interaction of copper phthalocyanine (CuPc) and volatile organic compounds (VOCs, benzene) has been studied by density functional theory (DFT). The VOCs molecule in this study was benzene on the top of copper phthalocyanine molecule. The DFT used for geometry optimization of these molecules and the electric field was applied perpendicularly the planar molecules with the range of 3 – 10 $MVcm^{-1}$. The results of applied electric field lead to change of molecular orbital energy level with calculating the half splitting of Homo and LUMO (apparent transfer integral). The Monte Carlo technique and Marcus-Levich-Jortner (MLJ) formalism for calculating the hopping rate from apparent and effective transfer integral were used in this simulation. Sum of hopping distance and hopping time were collected with simulation 10^9 cycles in this range of applied electric field for calculating the carrier mobility. Other statistic parameters were collected for example, the number of carrier hopping along and against electric field. The result of carrier mobility for CuPc gas sensor of benzene was higher than carrier mobility of pure CuPc along b direction.

Keywords: CuPc; benzene; DFT; hopping model; carrier mobility

1. Introduction

The organic semiconductor can be used in photovoltaic cell [1], liquid crystal display [2], electroluminescent devices [3] and organics field effect transistor [4 – 6] which base on phthalocyanine such as ZnPc, CuPc etc. The hopping model [7 – 9] can be used to study the carrier transport in organic semiconductors in both one dimension [8, 10] and three dimensions [11]. The organic semiconductors include both energetic disorder and polaronic contributions [12] for the carrier transfer can be applied by Miller-Abrahams formalism [13] and Marcus formalism [14]. The valence and conduction energy band edge are major properties of metal phthalocyanine (MPc) [15] with using in hopping transport to calculate hopping rate by Marcus formalism [14]. In the experiment CuPc was used as an active layer of bottom contact organic thin film transistors device to test current–voltage characteristics for the gas sensing properties [16] and for hydrogen sensor based on CuPc with palladium admixture measurement by the resistance [17]. In our calculation the hopping model is modified to study the carrier mobility for applied to gas sensor. The detail of calculation, the result of calculation and the conclusion are described in the next section.

2. Theoretical methodology

The molecule interaction between CuPc and benzene can be described by charge transport along the stack of these molecules. The key features of our approach are consisted of two works. The first is to evaluate at the quantum-chemical level the rate of charge transfer between two adjacent molecules in the presence of an applied external electric field. The second is to run Monte Carlo simulations based on the calculated transfer rates to estimate charge mobility.

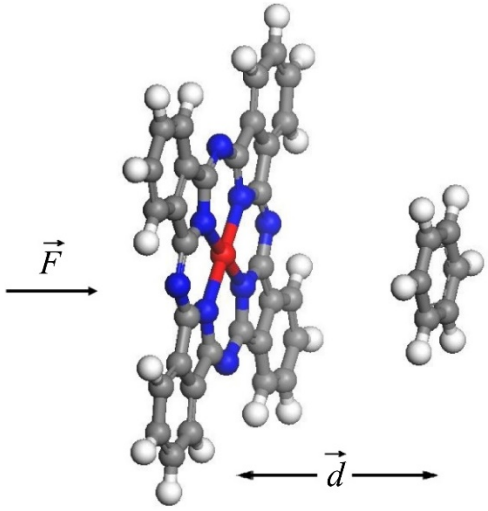

Fig. 1 Molecules orientation of CuPc and benzene with distance d Angstrom and electric field applied along z direction for the red, blue, gray and white circle are represented the atom of Cu, N, C and H respectively.

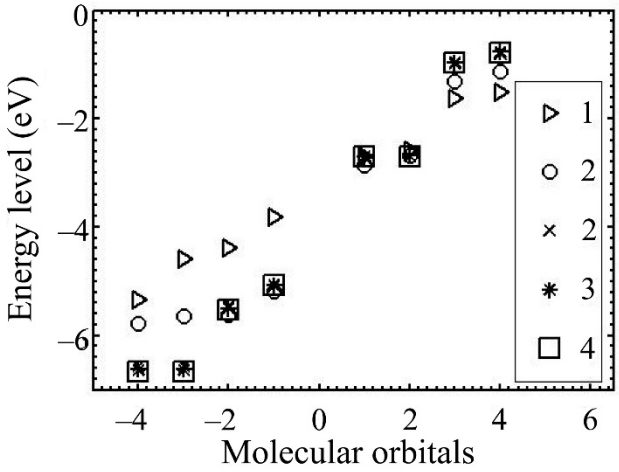

Fig. 2 The result of 1st to 4th molecular orbitals by DFT calculation for conduction band (–1 to –4) and the valance band (1 to 4) with vary distance of CuPc and benzene from 1 to 4 Å under the applied electric field 5.14 $MVcm^{-1}$.

The molecules of CuPc and benzene with constructed in three dimensions coordinate system can be presented in Fig. 1. In this figure each atoms of Cu, N, C and H can be represented by the color of red, blue, gray and white respectively. The benzene molecule constructed on the top of CuPc in the z direction and the electric field is applied in the same direction.

The geometry optimization of CuPc and benzene can be used DFT to calculate with the basis set of B3LYP/3-21G in GAMESS software. The stack of molecule is applied in this calculation with varied

electric field. The result can be calculated electronic molecular orbital can be shown in Fig. 2 and Table 1 for the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). HOMO interact can generate a valence band while interactions among LUMO for a conduction band. LUMO and HOMO are used in the carrier transport for electron and hole respectively. The majority carrier is hole in organic semiconductor, therefore; HOMO is considered only.

Table 1 The result of molecular orbitals by DFT calculation for conduction band and the valance band with vary distance of CuPc and benzene from 1 to 10 Å under the applied electric field 5.14 $MVcm^{-1}$.

Distance of two molecules (Å)	Energy level of the molecular orbital							
	–4	**–3**	**–2**	**–1**	**1**	**2**	**3**	**4**
1	–5.34	–4.60	–4.40	–3.82	–2.71	–2.59	–1.63	–1.51
2	–5.78	–5.64	–5.61	–5.19	–2.86	–2.69	–1.30	–1.13
3	–6.57	–6.57	–5.46	–5.09	–2.71	–2.70	–0.99	–0.81
4	–6.63	–6.63	–5.50	–5.07	–2.70	–2.69	–0.96	–0.77
5	–6.66	–6.66	–5.53	–5.08	–2.71	–2.71	–0.97	–0.78
6	–6.67	–6.67	–5.55	–5.09	–2.72	–2.72	–0.97	–0.79
7	–6.67	–6.67	–5.56	–5.09	–2.73	–2.72	–0.97	–0.79
8	–6.67	–6.67	–5.56	–5.09	–2.72	–2.72	–0.97	–0.79
9	–6.67	–6.67	–5.56	–5.09	–2.72	–2.72	–0.97	–0.79
10	–6.72	–6.71	–5.62	–5.15	–2.78	–2.78	–1.03	–0.85

Hopping rate of carrier can be calculated by Marcus theory, which implies that the charge is localized on the donor D prior to an acceptor A after the following electron transfer: $D^- + A \rightarrow D + A^-$. For calculation, Marcus-Levich-Jortner (MLJ) formalism is used as follows [8]:

$$k_{hop} = \frac{2\pi}{\hbar} t^2 \frac{1}{\sqrt{4\pi\lambda_s k_B T}} \sum_{n=0}^{\infty} \exp[-s] \frac{S^n}{n!} \exp[-\frac{(\Delta G^o + \lambda_s + n\hbar\omega_i)^2}{4\lambda_s k_B T}]. \quad (1)$$

Where t is the effective transfer integral that reflects the strength of electronic interaction between the adjacent molecules, T is the temperature, λ_s is the external reorganization energy, S is Huang-Rhys factor, ΔG° is a driving force and n vibration level. For the driving force can calculate form $\Delta G^o = e\vec{F} \,.\, \vec{d}$ with the vector associated with the electric field ($\vec{F}$) and the vector connecting the centroid ($\vec{d}$) of the electronic distribution associated with the HOMO/LUMO level of the two molecules. In our model, DFT is used to calculate the apparent transfer integral (t') of the half splitting molecular level in HOMO. The effective splitting can be calculated by

$$2t = \sqrt{2t'^2 - (\Delta G^o)^2}. \quad (2)$$

The probability of carrier transfer can be written as

$$p_{\rightarrow} = \frac{k_{\rightarrow}}{k_{\rightarrow} + k_{\leftarrow}}, \tag{3}$$

where $k_{\rightarrow}$ and $k_{\leftarrow}$ are hopping rate of carrier along and against of applied electric field. The Monte Carlo technique is used to choose the final state of carrier by generating random number between 0 and 1 if it is less than probability in equation (3) the carrier can be hoped otherwise the carrier remains at the initial position. In the calculation, the generating random number is used from "Numerical Recipes in fortran77: the art of scientific computing" for this standard subroutine to make sure that the random number is normal distribution.

The hopping cycles in our simulation, the value of simulated 10^9cycles is described in next section and the carrier mobility can be calculated by

$$\mu = \frac{d}{\tau F}. \tag{4}$$

Where d is the total hopping distance, F is the magnitude of applied electric field, τ is the sum of carrier hopping time that calculated from inverse of hopping rate.

3. Results and Discussion

In the calculation, the cycle of Monte Carlo simulation is tested by the tolerance of mobility for the applied electric field 5.14 MVcm^{-1}. The number of hopping in the simulation with the range of 10 – 10^9 cycles leads to the tolerance of mobility from 34.85% to 0.0004% respectively that show in Fig. 3(a). In the model simulation, the carrier

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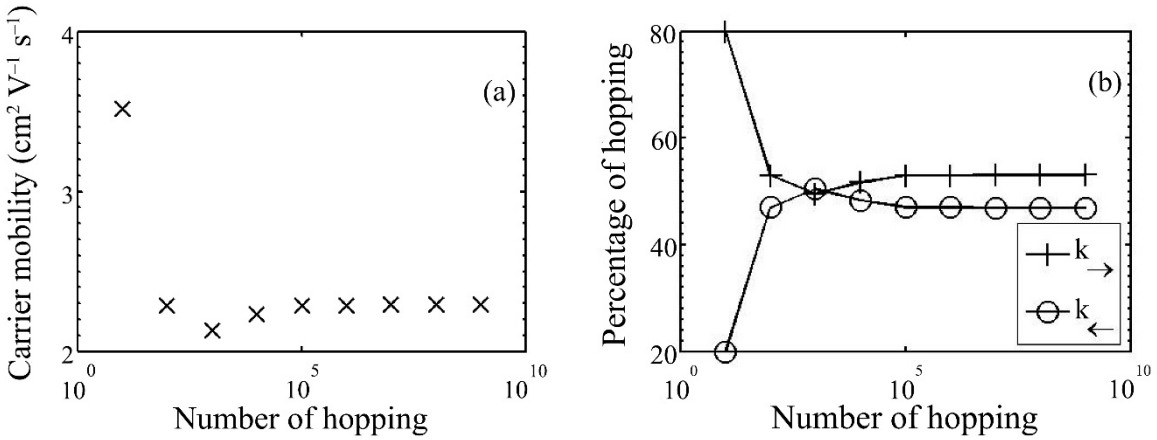

Fig. 3 The relation between carrier mobility (a) and percentage of hopping (b) as a function of hopping number.

Table 2 The result of calculation for apparent (t') transfer integral, driving force (ΔG°), effective (t) transfer integral, hopping rate of hole along electric field ($k_{\rightarrow}$) and hopping rate of hole against electric field ($k_{\leftarrow}$) as a function of applied electric field.

F (×MVcm^{-1})	t'_{HOMO} (×10^{-3}eV)	ΔG° (×10^{-3}eV)	t_{HOMO} (×10^{-3}eV)	$k_{\rightarrow}$ (s^{-1})	$k_{\leftarrow}$ (s^{-1})
3.09	185.45	92.56	179.58	907.78E+12	852.27E+12
3.60	185.45	107.99	177.41	907.69E+12	831.9E+12
4.11	185.45	123.41	174.88	907.60E+12	808.40E+12
4.63	185.58	138.84	172.11	908.84E+12	783.08E+12
5.14	185.58	154.27	168.79	908.75E+12	753.27E+12
5.66	185.58	169.70	165.05	908.66E+12	720.31E+12
6.17	185.72	185.12	161.01	909.91E+12	685.53E+12
6.68	185.72	200.55	156.32	909.81E+12	646.26E+12
7.20	185.85	215.97	151.26	911.06E+12	605.18E+12
7.71	185.85	231.40	145.45	910.97E+12	559.60E+12
8.23	185.99	246.83	139.15	912.21E+12	512.20E+12
8.74	185.99	262.25	131.90	912.12E+12	460.31E+12
9.26	185.99	277.68	123.76	912.03E+12	405.25E+12
9.77	186.13	293.11	114.74	913.27E+12	348.38E+12
10.28	186.13	308.53	104.14	913.18E+12	287.01E+12

DFT with the basis set of B3LYP/3-21G is used to calculate half splitting (apparent transfer integral, t') HOMO at applied electric field 5.14 MVcm^{-1} along z direction (shown in Fig. 1). The vary distance between CuPc and benzene molecule from 1 to 10 Å show in Fig. 4. The minimum energy of apparent transfer integral in the model is occurred at 3 Å. This value is used to study carrier behavior as a function of electric field with applying for gas sensor.

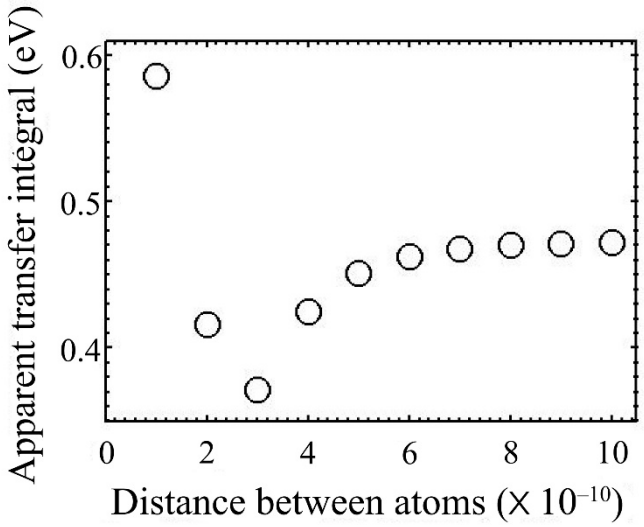

Fig. 4 Apparent transfer integral (t') of molecules CuPc and benzene with distance for applied electric field 5.14 MVcm^{-1} along z direction.

The field dependence of the calculated transfer integrals is analyzed by computing the apparent splitting for a dimmer of CuPc and benzene molecules are separated by 3 Å. The range of electric field

varying from 3 – 10 $MVcm^{-1}$ oriented perpendicular to the molecular planes (see Table 2). The extracted effective splitting with equation 2 was found to be affected by the magnitude of the electric field. This can be rationalized by the fact that the electronic distributions in the HOMO levels are perturbed for such an orientation of the electric field. As a result, the transfer integrals are kept changing in the Monte Carlo simulations when the magnitude of the electric field is varied.

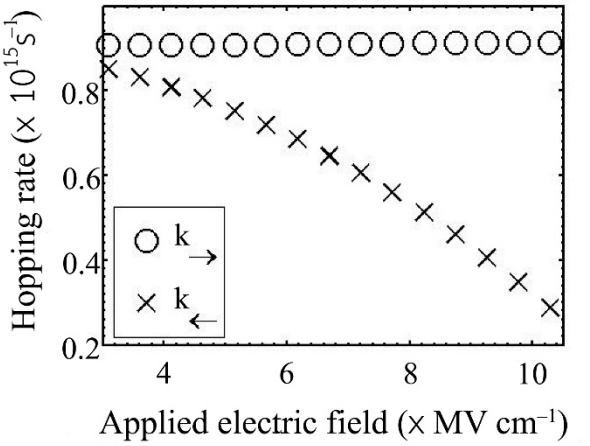

Fig. 5 The hopping rate of hole along electric field ($k_{\rightarrow}$) and hopping rate of hole against electric field ($k_{\leftarrow}$) as a function of applied electric field.

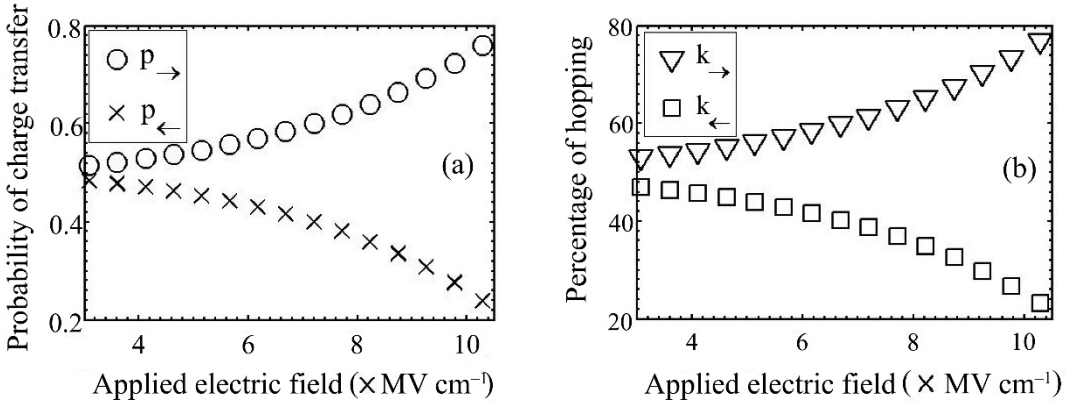

Fig. 6 The probability of charge transfer (a) with calculating from equation (3) and percentage of carrier hopping (b) with calculating from Monte Carlo simulation as a function of applied electric field.

The charge hopping process can be calculated by using Marcus-Levich-Jortner (MLJ) formalism in equation (1), for hopping rate of hole along electric field ($k_{\rightarrow}$) and hopping rate of hole against electric field ($k_{\leftarrow}$) as a function of applied electric field demonstrating in Table 2 and Fig. 5. The hopping rate for hole along electric field increases slightly but the hopping rate for hole against electric field is highly decreased. The carrier hopping 10^9 cycles for each cycle are simulated and used Monte Carlo technique. This technique generates the random number between 0 and 1 to choose the final state from the probability in equation (3). If the random number is less or equal to the final state probability, the carrier will be hopped and the simulation will be collected hopping distance and

hopping time. In the other way, the carrier remains at the initial position. The data in Fig. 6(a), the result was calculated from the analytic solution in equation (3) but in Fig. 6(b) the result was calculated from counting the number of carrier hopping along electric field ($k_{\rightarrow}$) and hopping against electric field ($k_{\leftarrow}$).

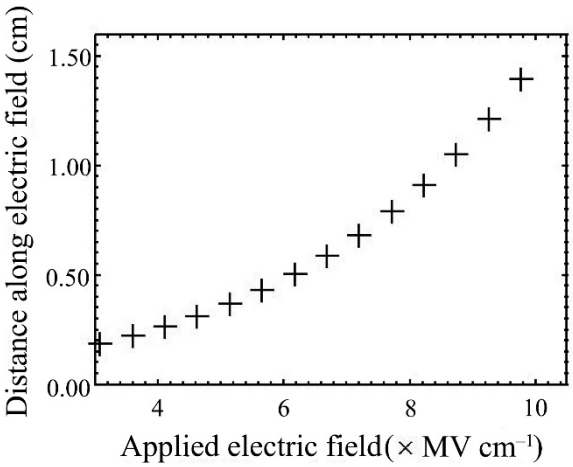

Fig. 7 The result of Monte Carlos simulation for total carrier displacement as a function of applied electric field.

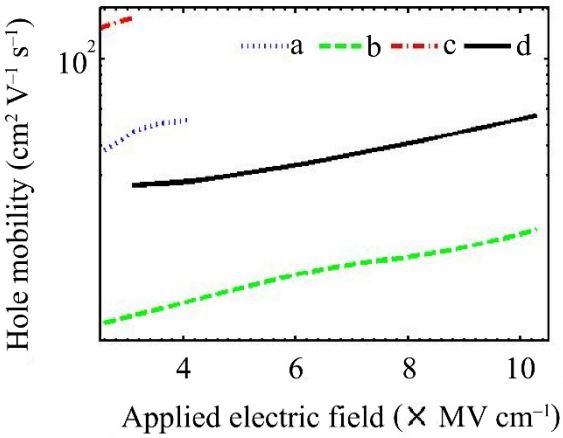

Fig. 8 The hole mobility for applied electric field along **a**, **b**, **c** crystal axis CuPc [10] and d for our calculation.

The result of total carrier displacement as a function of applied electric field can be shown in Fig. 7. Each hopping cycle the carrier will hop 3 Å. Therefore each simulation the carrier will travel in order of centimeter to show that the strong effect of applied electric field. The application of the CuPc for gas sensor of benzene can be demonstrated in Fig. 8. From the result of "Hole mobility of molecular β-copper phthalocyanine crystal" [10] it was studied about the carrier mobility along **a**, **b**, **c** direction of single crystal by Monte Carlo simulation. The result shows the electric field limitation of carrier mobility along **a** and **c** direction but it can be calculated the carrier along **b** direction. The CuPc is applied for benzene sensor and the carrier mobility is higher than the carrier along **b** direction.

4. Conclusion

In the calculation density functional theory was used to calculate the HOMO of CuPc and benzene molecules with applied electric field in the range of 3 to 10 $MVcm^{-1}$. The apparent transfer integral (half splitting of HOMO) was increased as a function of electric field with using to calculate the hopping rate by Marcus-Levich-Jortner formalism for the result of hopping rate in the order of 10^{14} s^{-1}. The hopping rate for carrier hopping along electric field was increased as a function of electric field but for carrier hopping against electric field was decreased from 8×10^{14} to 2×10^{14} s^{-1}. The major carrier hop along the electric field direction to get the result of simulation for the mobility was in the range of 20 to 50 $cm^2V^{-1}s^{-1}$ which was greater than the mobility of hole hopping in β-CuPc along **b** direction. From the result, CuPc hole mobility was applied to measure the benzene gas.

5. Acknowledgement

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