Density function theory study on structures and electronic properties of 2Meq2AlOPh and its derivatives

Yanju Ji¹, Xiaocun Liu, Gang Fu, Ying Chen, Fengxiang Wang and Junqing Zhao
School of Science, Shandong Jianzhu University, Jinan 250101, China
E-mail: jiyanju@sdjzu.edu.cn

Abstract. Structures and electronic properties of 2Meq2AlOC₆H₄R (R=CN, Cl, H, OMe, NMe₂) have been studied in the scheme of density function theory with the B3LYP and the 6-31G (d) basis set. The substitutions of the electron-withdrawing groups (CN, Cl) increase the band gap while the substitutions of the electron-donating groups (OMe, NMe₂) decrease the gap. The substitutions of electron-withdrawing groups enhance the electron injection ability. In addition, the vertical ionization energies (IEV), the vertical electronic affinities (EAV) and reorganization energies of 2Meq2AlOPh and its derivatives are calculated in the work. All complexes are better electron transport materials.

1. Introduction
Since the discovery of Organic light-emitting device (OLEDs) by Tang C W [1] and Burroughes J H [2], OLEDs receive much attention due to its unique properties [3-8]. Tris (8-hydroxyquinoline) aluminum (Alq₃) has been a popular compound because of its green emission, good electron mobility, and thermal stability up to 350°C [9]. Numerous studies, both theoretical and experimental, have been carried out on the derivatives of Alq₃ [10-15]. As an efficient green emitter with emission maximum in the range of 526 nm, Alq₃ could meet the requirement of green OLEDs. Until now, however, blue electroluminescent materials derived from organometallic complexes are rare. Leung et al. [16] synthesized a high-efficiency blue dye bis (2-methyl-8-quinolinolato) aluminum (III) hydroxide complex (2MAIq₂OH). Another complex, bis (2-methyl-8-quinolinolato) (phenolate) aluminum (III) (2Meq₂AIOPh), showed a higher chemical stability [17, 18].

In general, an OLED consists of a series of sequentially-deposited organic thin films sandwiched between two electrodes. Electrons which are injected from cathode should fill in the lowest unoccupied molecular orbital (LUMO) while holes injected from the anode should concentrate on the highest occupied molecular orbital (HOMO). The electrons can recombine the holes to form electron-hole pairs to emit light. The information about the ease of the electron injection can be given by discussing the injection energy from cathode to the complex.

In the present study, we report the theoretical study on the geometry structures and electronic structures of 2Meq₂AlOC₆H₄R (R=CN, Cl, H, OMe, NMe₂). Comparison of charge transfer properties of the five complexes was carried out.

¹ Address for correspondence: Yanju Ji, School of Science, Shandong Jianzhu University, Jinan 250101, China. E-mail: jiyanju@sdjzu.edu.cn.
2. Calculation method and models
The molecular models used in our calculations are given in figure 1, where the labels A-C represent the three different ligands. The geometries of 2Meq$_2$AlOCI$_4$$_4$H$_4$R (R=CN, Cl, H, OMe, NMe$_2$) in their neutral, cationic, and anionic states were fully optimized using Becke’s three-parameter hybrid functional [19] combined with the Lee, Yang and Parr (LYP) correlation functional [20], denoted B3LYP [21] with the 6-31G(d) [22-25] basis, which have given reliable results for organic materials [26-28]. The frontier orbital energies and molecular orbital maps of HOMO and LUMO for complexes were also given using B3LYP with 6-31G (d). All the calculations results have been performed using Gaussian 03 package [29].

![Figure 1.](image)

**Figure 1.** (a) The geometry of 2Meq$_2$AlOPh. (b) Calculation models of 2Meq$_2$AlOPh and its derivatives with labels A-C for three ligands.

3. Results and discussion

3.1. Molecular geometries
Some optimized bond lengths for 2Meq$_2$AlOPh and its derivatives are presented in table 1. In comparison with complex c (2Meq$_2$AlOPh), there are slightly geometrical changes in the four derivatives. The Al-N$_A$ bond is predicted to be negligible shortened in complex a while lengthened in complexes b, d, and e. The Al-N$_B$, Al-O$_A$, Al-O$_B$ bonds are predicted to be shorted while the Al-O$_C$ bonds are lengthened in complexes a and b. The bond lengths of Al-N and Al-O of complex d are almost similar as in e.

![Table 1.](image)

**Table 1.** Selected optimized bond lengths in angstrom (Å) for 2Meq$_2$AlOPh and its derivatives at the B3LYP/6-31G* level

| Parameters | a   | b   | c   | d   | e   |
|------------|-----|-----|-----|-----|-----|
| Al-N$_A$   | 2.086 | 2.089 | 2.087 | 2.090 | 2.091 |
| Al-N$_B$   | 2.073 | 2.075 | 2.076 | 2.078 | 2.078 |
| Al-O$_A$   | 1.815 | 1.817 | 1.820 | 1.820 | 1.820 |
| Al-O$_B$   | 1.815 | 1.818 | 1.820 | 1.821 | 1.822 |
| Al-O$_C$   | 1.776 | 1.768 | 1.764 | 1.761 | 1.761 |

3.2. Frontier molecular orbitals
The energies for the frontier molecular orbital energies and energy gaps of complexes a-e are shown in figure 2 and the molecular orbital maps of HOMO and LUMO for complexes b-d are shown in figure 3. The LUMO levels in complexes a-e are not significantly changed while the HOMOs are changed significantly. We reason that due to the molecular orbital maps of HOMO and LUMO for the complexes. The LUMOs are mostly localized on A and B but rarely on C while the HOMOs are
localized mostly on C. The metal Al only plays a role in supporting and restricting ligand. It doesn’t contribute to HOMO and LUMO.

The substitutions of electron-withdrawing groups (CN, Cl) increase the gap, while the substitutions of an electron-donating group (OMe, NMe₂) decrease the band gap. Complex a shows the highest HOMO-LUMO gap of 3.74eV and complex e shows the lowest HOMO-LUMO gap of 2.87 eV. A gradual decrease in the HOMO-LUMO gap comes from electron-withdrawing groups to electron-donating groups, a>b>c>d>e. As already known, the magnitudes of the HOMO-LUMO gap correlate with the emission properties. The smaller the gap is, the longer the emission wavelength is. Thus, the substitutions of electron-withdrawing groups (CN, Cl) show blue shifts, while the substitutions of electron-donating group (OMe, NMe₂) show red shifts.

3.3. Electron injection
The information about the ease of the electron injection can be given by discussing the injection energy (E_{inj}) from a cathode (as in Al) to the complex. The E_{inj} is calculated as follow:

\[ E_{inj} = E_{LUMO} - E_{Al} \]  

where \( E_{LUMO} \) are the LUMO energies, \( E_{Al} \) is the work function of Al.

Obviously, a low LUMO energy is favorable for enhancing the electron injection ability. Since the LUMO energies (eV) of complexes a-e are -1.95, -1.82, -1.71, -1.68, -1.66 eV and the work function of Al is -4.3 eV [30], the injection energies are 2.35, 2.48, 2.59, 2.62 and 2.64 eV. For the five complexes, the order of the calculated E_{inj} is a<b<c<d<e. The substitutions of electron-withdrawing groups (CN, Cl) enhance the electron injection ability.
3.4. Reorganization energies

The charge transfer rate in the organic solid can be accounted for by the Marcus theory [31] via the following equation:

\[ K_{h/e} = \frac{V_{h/e}}{\hbar} \times \left( \frac{\pi}{\lambda_{h/e}kT} \right)^{1/2} \times \exp \left( -\frac{\lambda_{h/e}}{4kT} \right) \]  

(2)

where \( k \) and \( \hbar \), respectively, refer to the Boltzmann and Plank constant, \( T \) the temperature, \( V_{h/e} \) the electronic couplings between adjacent molecules and \( \lambda_{h/e} \) the reorganization energies for hole or electron carriers.

Obviously, the electron transfer rate is determined by two major parameters: \( V_{h/e} \) and \( \lambda_{h/e} \). It has reported that \( V_{h/e} \) shows a narrow range of values [32, 33], therefore, the charge transfer rate is dominated by the reorganization energies \( \lambda_{h/e} \). The smaller the reorganization energies, the better the carrier transfer properties. The hole/electron reorganization energies are as

\[ \lambda_h = IEV - HEP; \lambda_e = EEP - EAV \]  

(3)

where HEP is the hole extraction potential and EEP is the electron extraction potential.

The vertical ionization energies (IE\( _V \)), the vertical electronic affinities (EAV\( _V \)) and reorganization energies of 2Meq2AlOPh and its derivatives are shown in Table 2.

**Table 2.** Vertical ionization energies, vertical electronic affinities, hole/electron extraction potentials (HEP/EEP) and hole/electron reorganization energies (\( \lambda_h/\lambda_e \)) (in eV) for complexes a-e at the DFT/B3LYP/6-31G* level.

|     | a     | b     | c     | d     | e     |
|-----|-------|-------|-------|-------|-------|
| IE\( _V \) | 6.917 | 6.703 | 6.617 | 6.344 | 6.086 |
| EAV\( _V \) | 0.693 | 0.553 | 0.448 | 0.418 | 0.407 |
| HEP  | 6.797  | 6.530 | 6.461 | 5.667 | 5.128 |
| EEP  | 0.937  | 0.792 | 0.667 | 0.685 | 0.649 |
| \( \lambda_h \) | 0.120  | 0.173 | 0.156 | 0.267 | 0.956 |
| \( \lambda_e \) | 0.244  | 0.239 | 0.219 | 0.267 | 0.242 |

The calculated vertical ionization energy and vertical electronic affinity for 2Meq2AlOPh are 6.617 eV and 0.448 eV. In line with the change in their HOMO and LUMO, substitutions of electron-withdrawing groups increase the vertical ionization energy and vertical electronic affinity, while the substitutions of electron-donating groups decrease them. Both the vertical ionization energy and vertical electronic affinity for all of the complexes are in following order: \( a > b > c > d > e \).

The reorganization energies of the derivatives are a little higher than that of 2Meq2AlOPh for electron while the hole reorganization energies among all complexes are quite different. The hole reorganization energy of complex a is smaller than that of complex c. But the hole reorganization energies of complexes d and e are quite large. Based on equation (2), the smaller the reorganization energies, the better the carrier transfer properties. The calculated electron reorganization energies of derivatives are higher than that of 2Meq2AlOPh, but the effect is not significant. As a result, 2Meq2AlOPh and its derivatives are better electron transport materials.

4. Conclusions

The geometries and electronic structures of 2Meq2AlOC\( _6 \)H\( _4 \)R (R=CN, CI, H, OMe, NMe\( _2 \)) were fully optimized using B3LYP with 6-31G (d) set. The structures of derivatives change slightly. The LUMOs are mostly localized on A and B but rarely on C, while the HOMOs are localized mostly on C and the metal Al doesn’t contribute to HOMO and LUMO. The substitutions of electron-withdrawing groups increase the gap and enhance the electron injection ability. The vertical ionization energies, the
vertical electronic affinities and reorganization energies of 2Meq$_2$AlOPh and its derivatives are given. All complexes are better charge transport materials.

Acknowledgment

This work was supported by the National Natural Science Foundation of China under Grant Nos 11005070, 51042002 and 11075097, and the Natural Science Foundation of Shandong Province, China (ZR2009FM031).

References

[1] Tang C W and VanSlyke S A 1987 Appl. Phys. Lett. 51 913
[2] Burroughes J H, Jones C A and Friend R H 1988 Nature 335 137
[3] Burroughes J H, Bradley D D C, Brown A R, Marks R N, Mackay K, Friend R H, Burns P L and Homes A B 1990 Nature 347 539
[4] Forrest S R 1989 IEEE Circuits Device Mag. 5 33
[5] Adachi C, Tokito S, Tsutsui T and Saito S 1988 Jpn. J. Appl. Phys. 27 L269/L713
[6] Goetzberger A, Luther J and Willeke G 2002 Solar Energy Mater. Solar Cells 74 1
[7] Choi J H, Kim K H, Choi S J and Lee H H 2006 Nanotechnology 17 2246
[8] Sun Y, Giebink N C, Kanno H, Ma B, Thompson M E and Forrest S R 2006 Nature 440 908
[9] Chen C and Shi J 1998 Coord. Chem. Rev. 171 161
[10] Zhang J and Frenking G 2004 Chem. Phys. Lett. 394 120
[11] Gahungu G and Zhang J 2005 J. Phys. Chem. B 109 17762
[12] Wang W, Dong S, Yin S, Yang J and Lu J 2008 J. Mol. Struct. (THEOCHEM) 867 116
[13] Wu C C, Lin Y T, Wong K T, Chen R T and Chen Y Y 2004 Adv. Mater. 16 61
[14] Chan L H, Lee R H, Hsieh C F, Yeh H C and Chen C T 2002 J. Am. Chem. Soc. 124 6469
[15] Irfan A, Cui R H and Zhang J P 2009 Theor. Chem. Acc. 122 275
[16] Leung L M, Lo W Y, So S K, Lee K M and Choi W K 2000 J. Am. Chem. Soc. 122 5640
[17] Qiu Y, Shao Y, Zhang D and Hong X 2000 Jpn. J. Appl. Phys. 39 1151
[18] Shen Z, Burrows P E, Bulovic V, Forrest S R and Thompson M E 1997 Science 276 2009
[19] Becke A D 1993 J. Chem. Phys. 98 5648
[20] Lee C, Yang W and Parr R G 1988 Phys. Rev. B 37 785
[21] Stephens P J, Devlin F J, Chabalowski C F and Frisch M J 1994 J. Phys. Chem. 98 11623
[22] Hariharan P C and Pople J A 1974 Mol. Phys. 27 209
[23] Gordon M S 1980 Chem. Phys. Lett. 76 163
[24] Frisch M J, Pople J A and Binkley J S 1984 J. Chem. Phys. 80 3265
[25] Foresman J B, Head-Gordon M, Pople J A and Frisch M J 1992 J. Phys. Chem. 96 135
[26] Zhang R Q, Lu W C, Lee C S, Hung L S and Lee S T 2002 J. Chem. Phys. 116 8827
[27] Irfan A, Cui R and Zhang J 2010 J. Mol. Struct. (THEOCHEM) 956 61
[28] Gahungu G, Zhang J, Ntakarutimana V and Gahungu N 2010 J. Phys. Chem. A 114 652
[29] Frisch M J et al. 2003 GAUSSIAN 03 Revision B. 03 (Pittsburgh: Gaussian Inc.)
[30] Michaelon H B 1997 J. Appl. Phys. 48 4729
[31] Marcus R A and Sutin N 1985 Biochim Biophys Acta 811 265
[32] Nelsen S F, Triebel D A, Ismagilov R F and Teki Y 2001 J. Am. Chem. Soc. 123 5684
[33] Nelsen S F and Blomgren F 2001 J. Org. Chem. 66 6551