Density function theory study on structures and electronic properties of 2Meq$_2$AlOPh and its derivatives

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Abstract. Structures and electronic properties of 2Meq$_2$AlOC$_6$H$_4$R (R=CN, Cl, H, OMe, NMe$_2$) 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, NMe$_2$) decrease the gap. The substitutions of electron-withdrawing groups enhance the electron injection ability. In addition, the vertical ionization energies (IE$_V$), the vertical electronic affinities (EA$_V$) and reorganization energies of 2Meq$_2$AlOPh 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 (Alq$_3$) has been a popular compound because of its green emission, good electron mobility, and thermal stability up to 350ºC [9]. Numerous studies, both theoretical and experimental, have been carried out on the derivatives of Alq$_3$ [10-15]. As an efficient green emitter with emission maximum in the range of 526 nm, Alq$_3$ 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 (2MAlq$_2$OH). Another complex, bis (2-methyl-8-quinolinolato) (phenolate) aluminum (III) (2Meq$_2$AlOPh), 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 2Meq$_2$AlOC$_6$H$_4$R (R=CN, Cl, H, OMe, NMe$_2$). Comparison of charge transfer properties of the five complexes was carried out.

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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 $2Meq_2AlOC_6H_4R$ (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].
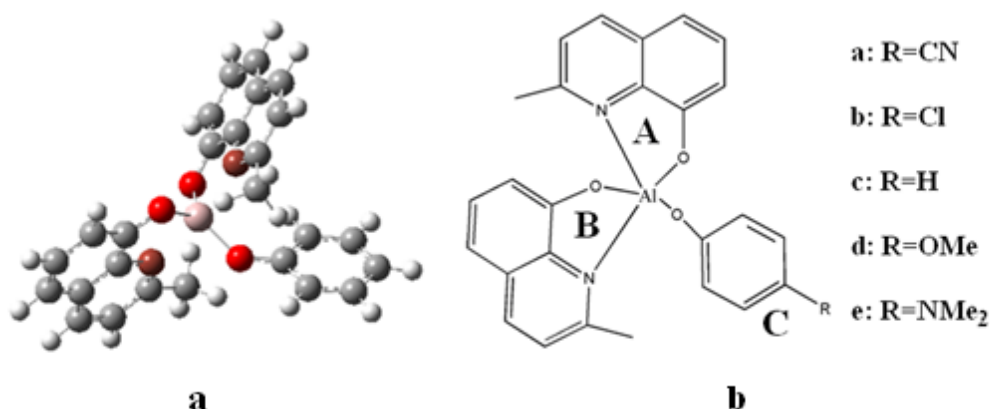

Figure 1. (a) The geometry of $2Meq_2AlOPh$. (b) Calculation models of $2Meq_2AlOPh$ and its derivatives with labels A-C for three ligands.

3. Results and discussion

3.1. Molecular geometries

Some optimized bond lengths for $2Meq_2AlOPh$ and its derivatives are presented in table 1. In comparison with complex c ($2Meq_2AlOPh$), 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. Selected optimized bond lengths in angstrom (Å) for $2Meq_2AlOPh$ 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, NMe$_2$) 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, NMe$_2$) show red shifts.
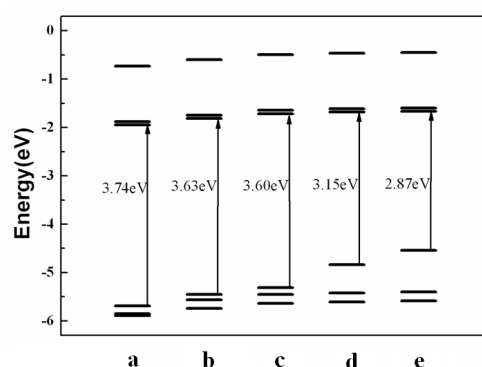

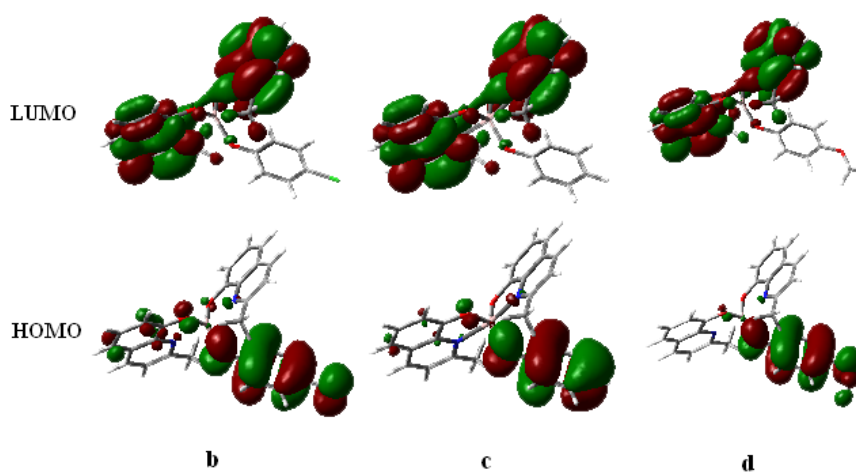**Figure 2.** HOMO-LUMO gap for complexes a-e.

Figure 3. Molecular orbital maps of HOMO and LUMO for complexes b-d.

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:

$$E_{inj}=E_{LUMO}-E_{Al} \tag{1}$$

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_{injs} 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:

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

where k and ℏ, 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

$$\lambda_h = IE_V - HEP; \ \lambda e = EEP - EA_V \tag{3}$$

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

The vertical ionization energies (IE_V), the vertical electronic affinities (EA_V) and reorganization energies of 2Meq$_2$AlOPh 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 (λ_h/λ_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
EA_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
λ_h	0.120	0.173	0.156	0.677	0.956
λ_e	0.244	0.239	0.219	0.267	0.242

The calculated vertical ionization energy and vertical electronic affinity for 2Meq$_2$AlOPh 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 2Meq$_2$AlOPh 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 2Meq$_2$AlOPh, but the effect is not significant. As a result, 2Meq$_2$AlOPh and its derivatives are better electron transport materials.

4. Conclusions

The geometries and electronic structures of 2Meq$_2$AlOC$_6$H$_4$R (R=CN, Cl, 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.

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