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Toward rational designing of n-type materials: Theoretical investigations of *mer*-Alq3 derivatives

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ABSTRACT

The ground state geometries of the CN and OCH_3 derivatives of the meridianal isomer of tris(8-hydroxyquinolinato)aluminum (*mer*-Alq3) were calculated by density functional theory. The absorption spectra were computed at the TD-PBE0/6-31G$*$ level. We have observed that position for substitution plays important role for absorption properties. The cyano derivatives make the LUMO energy levels lower and the electron affinity increase, thus these derivatives would enhance the electron injection ability. The ionization potentials and electron affinities showed that cyano derivatives would be better hole blockers than methoxy derivatives. The reorganization energies indicate that CN derivatives would enhance the electron mobility while introduction of OCH_3 has no effect in the enhancement of electron mobility. We explained the distribution of highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) on different individual ligands.

1. Introduction

In 1987, Tang and Van Slyke [1] reported the first efficient, low molecular weight organic light-emitting device (OLED) with two layers and using the metaloquinolate tris(8-hydroxyquinolinato)aluminum (Alq3) as the electron-transport material and emitting layer. In the following decades, OLEDs have become the highly competitive alternative of full color flat panel display [2–4]. There are two geometric isomers of Alq3, the facial tris(8-hydroxyquinolinato)aluminum (fac-Alq3) and meridianal (*mer*-Alq3) forms with *C3* and *C1* symmetries, respectively. The *mer*-Alq3 has become the prototype of a whole class of electroluminescent units currently in use in OLEDs [5]. Both experimental [6,7] and theoretical [7] studies indicate that the meridianal isomer is more stable energetically and generally the major constituent of thin films. Therefore, the calculations performed here will exclusively consider *mer*-Alq3. The electronic structures of *mer*-Alq3-like complexes can be tuned by adding substituents to quinolate ligand. By attaching electron donating group (EDG) to pyridine ring causes a blue shift in complex emission [8–10] while introduction to benzene ring causes a red shift [9,10].

Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) play important role in the charge transfer properties. Energy decomposition analysis that is the bond energy between the fragments of a molecular system into contributions associated with the various orbital and electrostatic interactions [11] of the bonding between the fragments AlL_2^+ (Al along with any two ligands among ligand-A, ligand-B, and ligand-C) and a single ligand L_i^- (L_i = A, B or C ligand) has been performed to explain the distribution of HOMO and LUMO on individual ligands. The preparation energy ΔE_{prep} and the interaction energy ΔE_{int} is known as bond energy ΔE (Eq. (1)).

$$\Delta E = \Delta E_{prep} + \Delta E_{int} = \Delta E_{prep,\ geo} + \Delta E_{prep,\ el} + \Delta E_{int} \quad (1)$$

The interaction energy ΔE_{int} is further decomposed into three physically meaningful terms.

$$\Delta E_{int} = \Delta E_{elst} + \Delta E_{pauli} + \Delta E_{orb} \quad (2)$$

ΔE_{elst} gives the electrostatic interaction energy between the fragments which are calculated with the frozen electron density distribution of A and B in the geometry of the complex AB. It can be considered as an estimate of the electrostatic contribution to the bonding interactions. ΔE_{pauli}, refers to the repulsive interactions between the fragments which are caused by the fact, that two electrons with the same spin cannot occupy the same region in space. The term comprises the four-electron destabilizing interactions between occupied orbitals. The last term in Eq. (2) gives the

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stabilizing orbital interactions, ΔE_{orb}, is the energy change due to the relaxation of the wave function to its final form through electron pair bonding, charge transfer and polarization. ΔE_{orb}, can be considered as an estimate of the covalent contributions to the bonding. Thus, the ratio $\Delta E_{\mathrm{elst}}/\Delta E_{\mathrm{orb}}$ indicates the electrostatic/covalent character of the bond. Detail can be found in Ref. [11]. With the aim to design blue and red shifted materials having high mobility, we have designed *mer*-Alq3 derivatives by substituting EDG (OCH_3) and electron withdrawing (EWD) group (CN) at different positions on all the ligands.

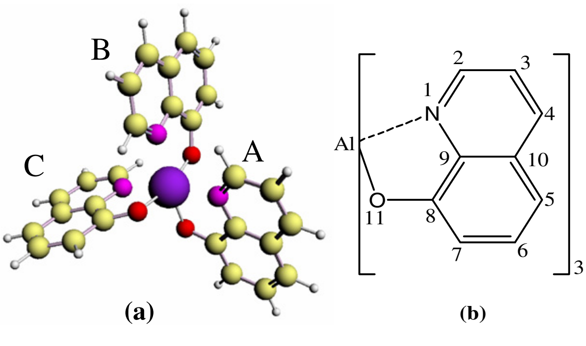
2. Computational details

All the calculations have been carried out with Gaussian 98 [12]. The structures of all the derivatives of *mer*-Alq3 (see labeling scheme in Fig. 1b) have been optimized in the ground state (S_0) at the B3LYP/6-31G$*$ level, which has been proved to be an efficient approach for *mer*-Alq3 and its derivatives [13–15]. The absorption spectra were calculated by time dependent density functional theory (TD-DFT) at PBE0/6-31G$*$ level which give good and accurate results as compared to B3LYP, BLYP, B3PW91 and SVWN [15]. The vertical and adiabatic ionization potentials, vertical and adiabatic electronic affinities and reorganization energies [16] have been calculated at B3LYP/6-31G$*$ level. Energy decomposition analysis has been carried out by using the B3LYP/DZP level [15]. Scalar relativistic effects were considered by using the zero-order regular approximation (ZORA) [17] on optimized structures at the B3LYP/6-31G$*$ level. The calculations for energy decomposition analysis have been carried out with the program package ADF [18].

3. Results and discussion

3.1. Molecular geometries

Fig. 1(a) is labeled with A–C designating the three different quinolate ligands of *mer*-Alq3. The structure is such that the central Al atom (+3 formal oxidation state) is surrounded by the three quinolate ligands in a pseudooctahedral configuration with the A- and C-quinolate nitrogens and the B- and C-quinolate oxygens trans to each other. The molecular models used in our calculations, obtained by systematic substitution in positions 3, 4, 5, and 6 (see labeling scheme) in each ligand are shown in Fig. 1. Table 1 present the selected geometrical parameters of the *mer*-Alq3 along with **1** and **5** as representatives, together with their corresponding pristine molecules, where both optimized and experimental results [19] are listed for comparison. Geometrical parameters from **1** to **8** can be found in Table S1.



n	Different ligands	Complexes
3	tris(3-cyano-8-hydroxyquinolinato)aluminum	**1**
4	tris(4-cyano-8-hydroxyquinolinato)aluminum	**2**
5	tris(5-cyano-8-hydroxyquinolinato)aluminum	**3**
6	tris(6-cyano-8-hydroxyquinolinato)aluminum	**4**
3	tris(3-methoxy-8-hydroxyquinolinato)aluminum	**5**
4	tris(4-methoxy-8-hydroxyquinolinato)aluminum	**6**
5	tris(5-methoxy-8-hydroxyquinolinato)aluminum	**7**
6	tris(6-methoxy-8-hydroxyquinolinato)aluminum	**8**

n= 3, 4,.., 6 substituted "H" position by "CN" and "OCH_3" as labeled in Fig. 1(b)

Fig. 1. (a) The geometry of *mer*-Alq3 with labels A–C for three quinolate ligands (b) the ligand labeling for *mer*-Alq3 substituted complexes considered in this work.

3.2. Frontier molecular orbitals (FMOs) analysis of S_0 states and absorption properties

The HOMOs are localized mostly on A-ligand while LUMOs are localized on B-ligand in *mer*-Alq3 and its derivatives [13–15]. The FMOs distributions of cyano and methoxy derivatives of *mer*-Alq3 at the S_0 states shown in Figs. 2 and S1, suggest a localization of molecular orbitals. The HOMOs and LUMOs in all the derivatives of *mer*-Alq3 showed the similar trend of localization at A and B ligands, respectively. The HOMO, LUMO, and gap energies of CN and OCH_3 are tabulated in Table 2, the trend of HOMOs energies (E_{HOMO}) is as follows: **7** > **6** > **5** > **8** > *mer*-Alq_3 > **2** > **1** > **4** > **3**, while in LUMOs energies (E_{LUMO}) is as: **6** > **5** > **7** > **8** > Alq_3 > **1** > **4** > **3** > **2**. The trend of gap energies (E_g) in *mer*-Alq3 derivatives is **6** > **5** > **8** > Alq_3 ~ **3** > **4** > **1** > **7** > **2**. The work function of Al is −4.3 eV [20] and the LUMO energy level of *mer*-Alq3 is −1.65 eV (see Table 2), the injection energy is around 2.65 eV (=−1.65 − (−4.3)) from the electrode Al to the *mer*-Alq3 surface. The barrier for electron transport across the interface is high, which indicates that *mer*-Alq3 has large energy barrier for charge injection, leading to somewhat high turn-on voltage for *mer*-Alq3. Therefore, it is necessary to lower the LUMO level to enhance the electron injection ability. From Table 2 it can be found that the CN derivatives effects make the LUMO energy levels lower; i.e., in **1** (0.94 eV), **2** (1.32 eV), **3** (0.98 eV) and **4** (0.96 eV).

The computed and experimental [21] absorption wavelengths have been reported in Table 2. The **1**, **2**, and **7** are red shifted, i.e., 28 nm, 96 nm and 52 nm while **3** and **6** are blue shifted, i.e., 8 nm and 32 nm, respectively. The **4**, **5**, and **8** are negligible blue shifted toward absorption wavelengths. The position for substitution plays important role as we have observed that EWD group CN at position 3 and 4 show red shift while substitution at position 5 lead to blue shift which is in good agreement with Burrows et al. [22]. It has been observed that EDG on pyridine ring causes blue shift while on benzene ring lead to red shift; our theoretical investigations are in good agreement with already reported work [8–10]. Generally, the complexes having higher energy gap than parent molecule show blue shift while small energy gap derivatives show red shifts.

3.3. Charge transfer properties

The charge transport can be depicted by a particle diffusion process [23,24] coupled with the Marcus theory of the electron transfer rate for a self-exchange reaction process [25–27].

$$K = V^2/h(\pi/\lambda k_B T)^{1/2}\exp(-\lambda/4k_B T) \tag{3}$$

The intermolecular transfer integral (V) and the reorganization energy (λ) are the main parameters that determine self-exchange electron-transfer (ET) rate. The reorganization energy is further divided into two parts: λ_1 and λ_2, where λ_1 corresponds to the geometry relaxation energy of one molecule from neutral state to charged state, and λ_2 corresponds to the geometry relaxation energy from charged state to neutral one [28,29].

$$\lambda = \lambda_1 + \lambda_2 \tag{4}$$