

# Energy Partitioning Analysis of the Chemical Bonds in *mer*-Mq3 (M = Al<sup>III</sup>, Ga<sup>III</sup>, In<sup>III</sup>, Tl<sup>III</sup>)

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**Abstract.** Geometries of ground states of *mer*-tris(8-hydroxyquinolino)metal (Mq3, M=Al<sup>3+</sup>, Ga<sup>3+</sup>, In<sup>3+</sup>, Tl<sup>3+</sup>) are optimized by B3LYP/6-31G(d) methods. The bonding interactions between the metal fragment Mq2 and each single ligand q have been analyzed with the energy decomposition scheme. The calculated results suggest that the HOMO and LUMO distribution fashion can be simply traced back to the lowest electrostatic attractive and highest orbital interaction energy between fragments A-quinolate ligand and Mq2 and B-ligand and Mq2, respectively.

**Keywords:** energy partitioning analysis, Mq3, FMO distribution fashion.

## 1 Introduction

Tris(8-hydroxyquinolino)aluminum, Alq3, is the mile stone for the development of organic light-emitting diode (OLED), which was used in the first OLED [1]. The majority of the molecular properties of metaloquinolate work carried out thus far has been on the ground-state (S<sub>0</sub>) [2-5] and first excited state (S<sub>1</sub>) [6,7] characteristics of Alq3. Mq3 has two geometric isomers, the facial (*fac*-Mq3) and meridional (*mer*-Mq3) forms, respectively. The energy partitioning analyses (EPA) method has recently been used in systematic investigations of the nature of the chemical bond in main-group and transition metal compounds [8]. In order to explore the difference of individual ligands from chemical bond point of view, energy partitioning method has been applied to the series of complexes *mer*-Mq3 as shown in Fig. 1, as a series study of our previous works [9,10].

## 2 Methodology

The calculations for *mer*-Mq3 (Fig. 1) described here were carried out by the same methods as described previously [9,10]. The structure of *mer*-Mq3 in S<sub>0</sub> state was optimized using the B3LYP functional with 6-31G(d) basis set for C, H, O, N, Al(III) Ga(III) and Stuttgart RLC ECP for In(III) and Tl(III), respectively. In order to explore the difference of individual ligands from chemical bond point of view, EPA was applied to the series of complexes.

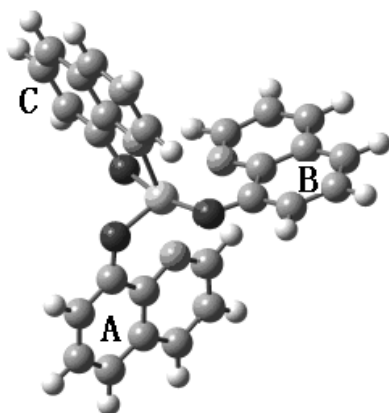


Fig. 1. The geometry of *mer*-Mq<sub>3</sub> with labels A-C for three q ligands (M=Al, Ga, In, Tl)

### 3 Results and Discussion

#### 3.1 The Optimized Structure Analyses of S<sub>0</sub> for *mer*-Mq<sub>3</sub>

The optimized structures for these complexes are listed in Table 1 (the results for Al and Ga complexes see our previous results [9]). For each complex, the bond lengths for O-M in ligand A are shorter than those in ligands B and C. The bond lengths of O-M are shorter than those of N-M and increase with their atomic numbers as O-Al < O-Ga < O-In < O-Tl. The bond angles of O-M-O and N-M-N decrease with their atomic numbers as O(N)-Al-O(N) > O(N)-Ga-O(N) > O(N)-In-O(N) > O(N)-Tl-O(N).

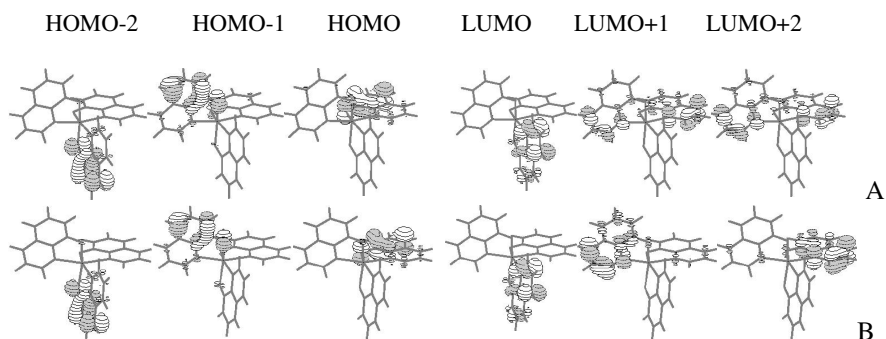
**Table 1.** Selected optimized bond lengths (Å) and bond angles (°) for *mer*-Mq<sub>3</sub> (M= In<sup>III</sup>, Tl<sup>III</sup>) by B3LYP/6-31G(d)

	Inq3-A	Inq3-B	Inq3-C	Tlq3-A	Tlq3-B	Tlq3-C
O-M	2.063	2.080	2.090	2.156	2.180	2.190
N-M	2.250	2.270	2.220	2.400	2.400	2.340
Oa-M-Nb		166.68			162.11	
Ob-M-Oc		157.08			151.69	
Na-M-Nc		166.30			162.72	
Oa-M-Na		77.61			74.26	
Ob-M-Nb		76.39			73.48	
Oc-M-Nc		77.32			74.69	

#### 3.2 The Frontier Molecular Orbitals (FMO) Analyses of S<sub>0</sub> for *mer*-Mq<sub>3</sub>

The FMO plots of *mer*-Mq<sub>3</sub> are shown in Figure 2 (the results for Al and Ga complexes see our previous results [9]). For each complex, the HOMO is mainly localized on one ligand (labeled A), while the two others are predominantly localized on the other ligands (C and B respectively for HOMO-1 and HOMO-2). The most low-lying unoccupied molecular orbital (LUMO) is found to be mainly localized on

ligand B the two others (LUMO+1 and LUMO+2) being mainly localized on other two ligands (C and A), respectively, for Alq3 and Tlq3, while almost uniformly localized on the same other two ligands (C and A) for Gaq3 and Inq3.



**Fig. 2.** FMOs for the ground state ( $S_0$ ) of *mer*-Mq3 (M=In(A), Tl(B)) with small core (Isocontour value 0.05)

### 3.3 The Energy Decomposition Analyses for *mer*-Mq3 in $S_0$ States

Table 2 gives the most important results of the bonding analysis for the interactions between one quinolate ligand and corresponding Mq2 fragment for investigated systems, respectively.

**Table 2.** The ETS analysis for Mq2<sup>+</sup>+q<sup>-</sup> complexes at BP86/T2ZP (kcal/mol) for the ground states of *mer*-Mq3

	$\Delta E_{\text{int}}$	$\Delta E_{\text{Pauli}}$	$\Delta E_{\text{elstat}}$	$\Delta E_{\text{orb}}$	$\Delta E_{\text{elstat}} \%$	$\Delta E_{\text{orb}} \%$
Alq2-q <sub>A</sub>	-192.42	152.46	<b>-215.25</b>	<b>-129.62</b>	62.41	37.59
Alq2-q <sub>B</sub>	-190.80	157.09	<b>-219.11</b>	<b>-128.78</b>	62.98	37.02
Alq2-q <sub>C</sub>	-194.37	158.00	<b>-221.48</b>	<b>-130.89</b>	62.85	37.15
Gaq2-q <sub>A</sub>	-169.60	192.67	<b>-222.57</b>	<b>-139.70</b>	61.44	38.56
Gaq2-q <sub>B</sub>	-169.11	199.14	<b>-229.06</b>	<b>-139.19</b>	62.21	37.39
Gaq2-q <sub>C</sub>	-172.25	199.00	<b>-230.73</b>	<b>-140.52</b>	62.15	37.85
Inq2-q <sub>A</sub>	-164.49	185.09	<b>-224.02</b>	<b>-125.56</b>	64.08	35.92
Inq2-q <sub>B</sub>	-163.38	181.18	<b>-224.59</b>	<b>-119.97</b>	65.18	34.82
Inq2-q <sub>C</sub>	-166.92	184.15	<b>-228.34</b>	<b>-122.73</b>	65.04	34.96
Tlq2-q <sub>A</sub>	-148.20	180.50	<b>-196.28</b>	<b>-132.42</b>	59.72	40.28
Tlq2-q <sub>B</sub>	-148.56	176.16	<b>-197.74</b>	<b>-126.98</b>	60.89	39.11
Tlq2-q <sub>C</sub>	-156.01	180.42	<b>-202.14</b>	<b>-134.28</b>	60.08	39.92

The results given in Table 2 show the same tendency for all investigated complexes. The interaction energy  $\Delta E_{\text{int}}$  between the two fragments increases in the sequence as Alq2-q<sub>L</sub> < Gaq2-q<sub>L</sub> < Inq2-q<sub>L</sub> < Tlq2-q<sub>L</sub>. Moreover, the larger  $\Delta E_{\text{elstat}} \%$  (59.72-65.18%) over  $\Delta E_{\text{orb}} \%$  (34.82-40.28%) suggests that metal-ligand interactions have a larger electrostatic character than covalent character. For each complex, the

electrostatic interaction energy ( $\Delta E_{\text{elstat}}$ ) between  $q_A$  and  $Mq_Bq_C$  fragments is weaker than those of  $q_B$ - $Mq_Aq_C$  and  $q_C$ - $Mq_Aq_B$ , which may result in the HOMOs localizing on A-ring for  $S_0$  states. The orbital interaction term,  $\Delta E_{\text{orb}}$ , between  $q_B$  and  $Mq_Aq_C$  fragments is higher than those of  $q_A$ - $Mq_Bq_C$  and  $q_C$ - $Mq_Aq_B$ , which may correspond to the localization of LUMOs on B-ligands.

## 4 Conclusions

The same HOMO and LUMO distribution fashion for *mer*-Mq3 system can be simply traced back to the lowest electrostatic attractive and highest orbital interaction energy between fragments A-quinolate ligand and Mq2 and B-ligand and Mq2, respectively. Our results suggest that EPA may be a powerful approach to rationalize the distribution patterns of HOMO and LUMO for complexes consisting of metal ion and three same component ligands with  $C_1$  symmetry.

**Acknowledgment.** Financial supports from the NSFC (No.50473032) and NCET-06-0321.

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