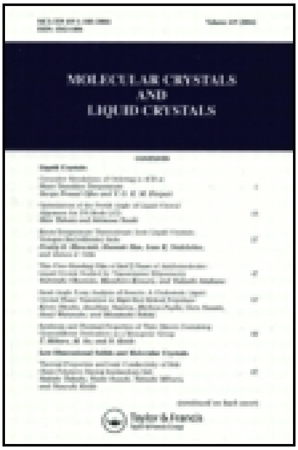

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Time-Dependent Density Functional Theory Study of the Al Complexes with Aromatic Ligands for Blue Organic Light-Emitting Diodes

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Aluminum(III) complexes with 8-hydroxyquinoline have attracted much attention because of their potential application in organic light emitting diodes (OLEDs) as green and blue emitting materials with the subtle effect of the substitution on the fluorescence and electroluminescent (EL) properties. The photoluminescence of aluminum(III) complexes [(tri(2′,2-dihydroxybiphenyl) aluminum(III)] have been studied as efficient fluorescence emitting materials [17]. In this paper, geometric and electronic properties of several Al complexes are studied to find the ligand effect related to the intensities of their absorptions and emissions using computational methods. In order to find a new highly efficient blue emitting materials, we have designed new Al complexes with aromatic ligands, [4,5-phenanthrenediol, 3,3′-dihydroxy-2,2′-binaphthalene, 2-(2′-phenol)-2-naphthol, and 1-(2′-phenol)-2-naphthol]. The geometry optimizations of the ground and the lowest excited electronic states were determined using HF/3-21G(d) and configuration interaction with single excitations (CIS) method. The vertical and adiabatic transition energies were calculated using time-dependent density functional theory (TD-DFT)

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with B1LYP/6-31G(d). As a result, we propose new blue fluorescent Al complexes of high luminescence efficiency.

Keywords: Al Complex; blue; OLED; TD-DFT

1. INTRODUCTION

Since the great discovery that organic material emits visible light in the multi-layered structure when a bias voltage is applied on the structure was reported by Tang *et al.* [1], intense researches and developments have been progressed in performance of organic light emitting diodes (OLEDs) [2–6] and in efficiency of emitting material [7–14]. Especially, for the advance of OLED performance, some layers have been added to enhance and to balance transporting mobility of holes and electrons [2,3].

Luminescent organometallic complexes have been shown to be particularly useful in OLEDs because of their relatively high stability and volatility [1]. Three 8-hydroxyquinoline(q) aluminum compound, tris(8-hydroxyquinoline) aluminum(III) (AlQ_3), is the most well known example and it has been used as a green emitter or an electron transport material in OLEDs. For full-color display applications, efficient red [7–9], green [10,11], and blue [12–14] emitters are needed. In spite of predominant advance of OLEDs, it is hard to find an appropriate blue emitting material because higher gap energy between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is needed for blue luminescence.

In this paper, geometric and electronic properties of AlP_3 and AlQ_3 complexes are studied using computational methods for the justification of the calculational method [15–17]. AlP_3 [(tri(2′,2-dihydroxybiphenyl) aluminum (III)] complex was reported to have higher photoluminescence (PL) intensity and bluisher than those of AlQ_3. From these calculations, newly designed blue fluorescent Al complexes with high luminescence efficiency are proposed.

2. DETAILS OF THE CALCULATIONS

Calculations on the ground electronic states of this complexes have been carried out using the Hatree-Fock(HF) method with a basis of 3-21G(d). The geometry optimization of the lowest excited electronic states was determined using configuration interaction with single excitations (CIS) method and 3-21G(d) basis set. The vertical and adiabatic transition energies were obtained from the calculation using the CIS method using Becke's one parameter hybrid functional with LYP correlation functional (B1LYP) density functional theory with the basis set of 6-31G(d) and Time-Dependent Density Functional Theory (TD-DFT) method with B1LYP/6-31G(d). All of calculations were carried out with Gaussian 98 W.

3. RESULT AND DISCUSSION

For the case of Al complex forming octahedral structure with nearest organic atoms of ligands, two types of isomers are known as *meridianal (mer-)* and *facial(fac-)*. Schematic structures of the tri(8-hydroxyquinoline) aluminum(III) (*mer*-AlQ_3) and the tri(2,2′-dihydroxybiphenyl) aluminum(III) (*mer*-AlP_3) are shown in Figure 1. The ground state geometries of *mer*- and *fac*- structures of AlQ_3 and AlP_3 are calculated with HF/3-21G(d), where the total energies of *mer*- and *fac*-AlQ_3's are –1653.96 a.u. and –1653.95 a.u. Also total energies of *mer*- and *fac*-AlP_3's are –2059.01 a.u. and –2058.91 a.u. Therefore, *meridianal* structure in both complexes of AlQ_3 and AlP_3 is more stable than *facial* structure.

The molecular structures of the aluminum(III) complexes are shown in Figure 2(i). Aluminum(III) complexes are *mer*-Al-$(L)_3$ form, where L

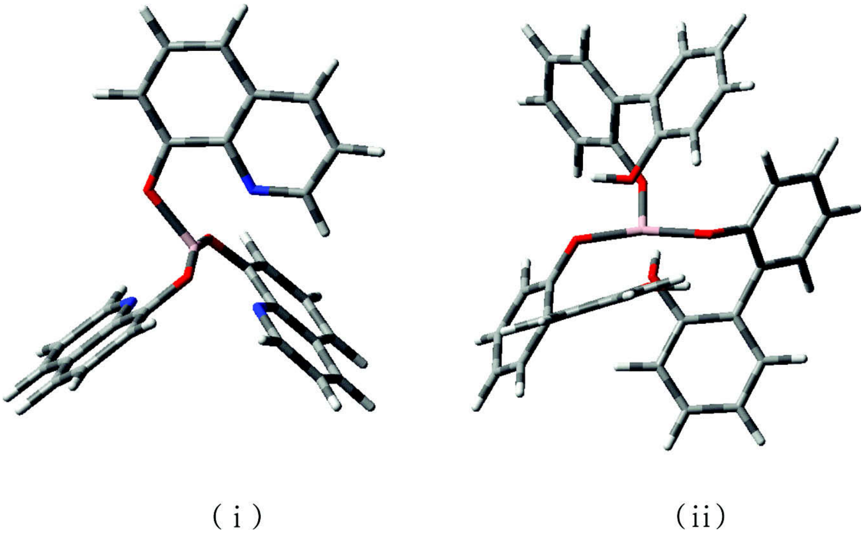
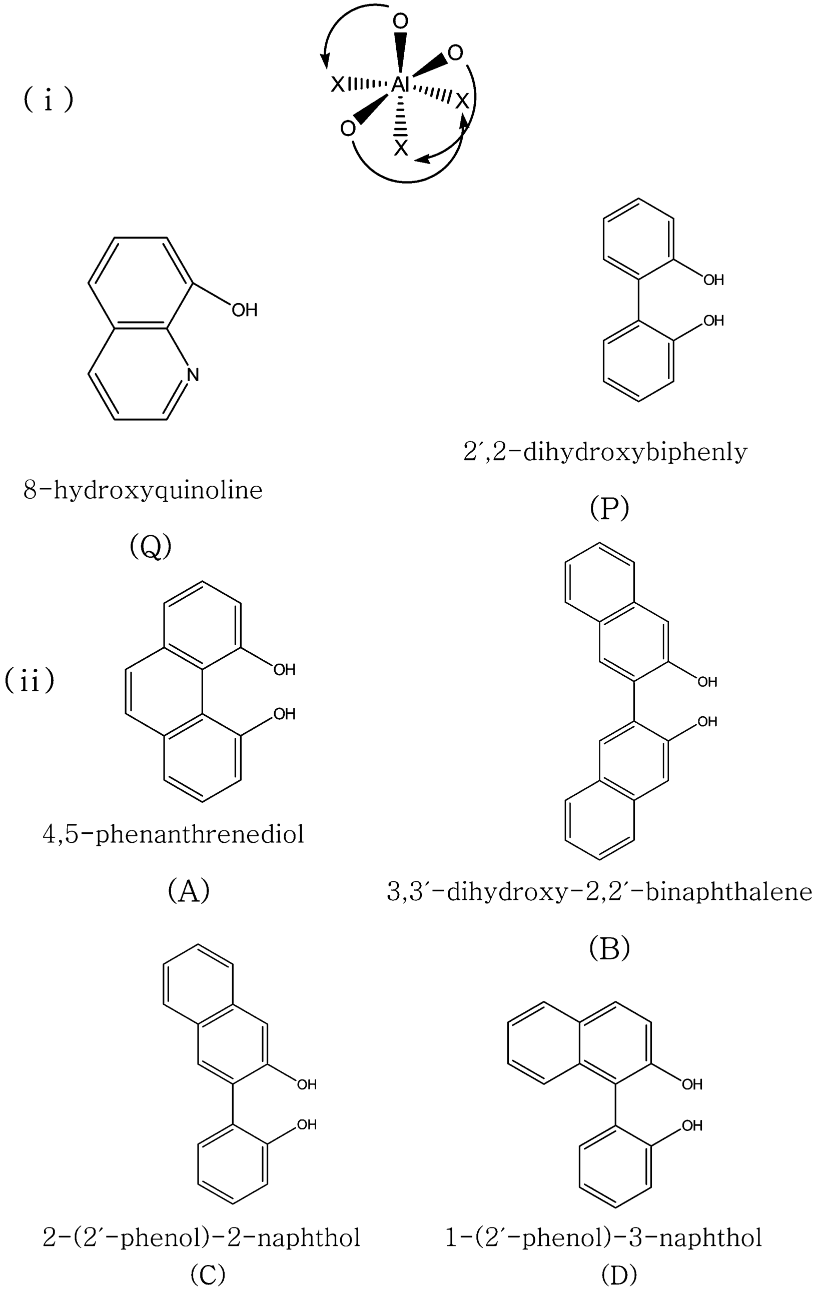


FIGURE 1 Geometrical structures of *mer*-AlQ_3 and *mer*-AlP_3.



8-hydroxyquinoline (Q)

2′,2-dihydroxybiphenly (P)

4,5-phenanthrenediol (A)

3,3′-dihydroxy-2,2′-binaphthalene (B)

2-(2′-phenol)-2-naphthol (C)

1-(2′-phenol)-3-naphthol (D)

FIGURE 2 Ligand structures of Al(III) complexes.

TABLE 1 Comparison of Calculated and Experimental Absorption/Emission Wavelength, Obtained after CIS(B1LYP/6-31G(d))//TD-DFT(B1LYP/6-31G(d))

		AlQ_3	AlP_3	AlB_3	AlC_3	AlD_3
Abs(nm)	CIS(B1LYP/6-31G(d))	395(0.02)	280(0.06)	346(0.02)	319(0.02)	305(0.13)
	TD-DFT(B1LYP/6-31G(d))	390(0.06)	280(0.06)	346(0.02)	319(0.02)	305(0.13)
	Exp*	388				
Ems(nm)	CIS(B1LYP/6-31G(d))	519(0.04)	333(0.2)	389(0.04) 357(0.24)	377(0.04)	362(0.14)
	TD-DFT(B1LYP/6-31G(d))	519(0.04)	333(0.2)	389(0.04) 357(0.25)	377(0.04)	364(0.14)
	Exp**	508(150)	378(593)			

Refer to: *(2001). *Chem. Mater., 13*, 2636.
**(2004). Yeh-Fang Duann & Guan-IN Chen. *Synth. Met.*, *144*, 121.

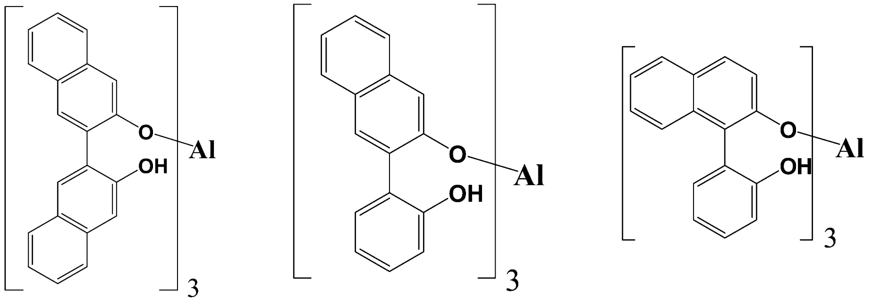
stands for one of 8-hydroxyquinoline (Q), 2,2′-dihydroxybiphenol (P), 4,5-phenanthrenediol (A), 3,3′-dihydroxy-2,2′-binaphthalene (B), 2-(2′-phenol)-3-naphthol (C) and 1-(2′-phenol)-2-naphthol(D) ligands, as shown in Figure 2(ii).

The photoemission spectra of AlQ_3 and AlP_3 excited by UV light of 300 nm were reported as 508 nm and 378 nm [18–20]. The calculated and experimental optical properties of AlQ_3 and AlP_3 are summarized in Table 1. The calculated PL wavelength of AlP_3 using TD-DFT is 333 nm, which rather disagrees with the experimental data of 378 nm. The experimental PL intensity of AlP_3 is nearly 4 times higher than that of AlQ_3 and the TD-DFT calculation shows similar results. Such an intensity difference also appears in ligand calculation. Calculated emissions of Q and P ligand are 370 nm and 312 nm, where their oscillation strengths are 0.05 and 0.41, respectively. The oscillation strength of P ligand is 8.2 times larger than that of Q ligand.

Even though AlP_3 have high intensity, the emission wavelength of AlP_3 is located out of blue region. Hence AlP_3 would not been applied directly as blue emitting material. So new ligands instead of P were designed to shift emissions bathochromically. Calculated data of

TABLE 2 Calculated Emission Wavelengths and Oscillation Strengths of Ligands, Obtained after TD-DFT(B1LYP/6-31G(d))

	Q	P	A	B	C	D
Ems	373(0.05)	312(0.41)	354(0.15)	351(0.47)	350(0.29)	355(0.24)



AlB$_3$ AlC$_3$ AlD$_3$

FIGURE 3 New candidated of Al (III) complexes considered in this study.

ligands are shown in Table 2. Emission wavelengths of P ligand and Q ligand are 312 nm and 370 nm, where oscillation strengths are 0.417 and 0.0013, respectively. Calculated emission wavelengths of newly proposed ligands, A, B, C and D, are located between those of P and

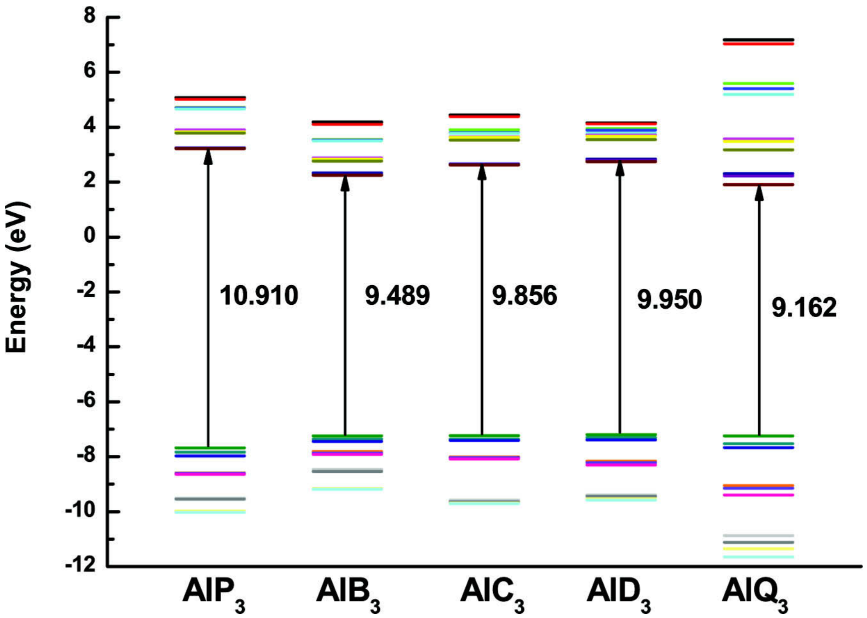


FIGURE 4 Schematic energy level diagrams of Al (III) complexes.

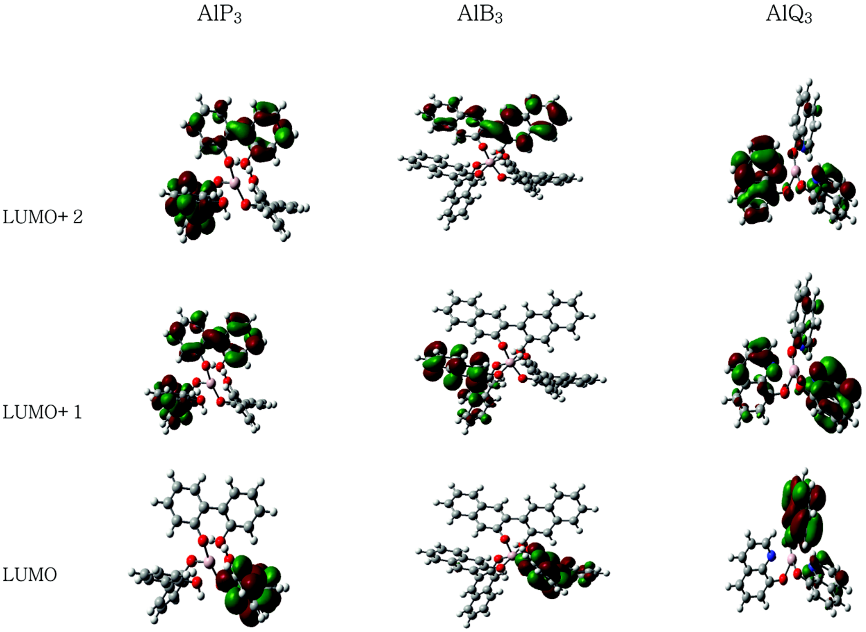


FIGURE 5 The lowest unoccupied molecular orbital (LUMO) structure of Al (III) complexes.

Q ligands, and oscillation strengths are properly high. Thus those are good candidates. New candidated complexes of those ligands are shown in Figure 3. The basic structure of AlP$_3$ was modified to approach blue region. The key point is that conjugation length is increased in ligand structure to shift the emission bathchromically. The geometry optimization were carried out with HF/3-21G(d) level. Figures 4, 5, and 6 show molecular orbital energies and structures of newly designed aluminum (III) complexes.

The calculated molecular orbital energies and contours of *mer*-AlQ$_3$ and *mer*-AlP$_3$ are shown in Figures 4, 5, and 6. It was shown that the electron population of HOMO and LUMO of AlQ$_3$ were localized on a different ligand. On the other hand, the electron population of HOMO level of AlP$_3$ is mainly delocalized on two ligands and gives larger Frank-condon factor. These result can explained that the PL intensity of AlP3 is nearly 4 times higher than that of AlQ$_3$. HOMO and LUMO energies of AlQ$_3$ are –7.252 eV and 1.910 eV. And the calculated HOMO and LUMO energies of AlP$_3$ are –7.682 eV and 3.227 eV. Hence, energy gabs of AlQ$_3$ and AlP$_3$ are 9.162 eV and 10.910 eV. Those gaps of AlB$_3$, AlC$_3$, and AlD$_3$ are 9.489 eV, 9.856 eV, and 9.950 eV, respectively.

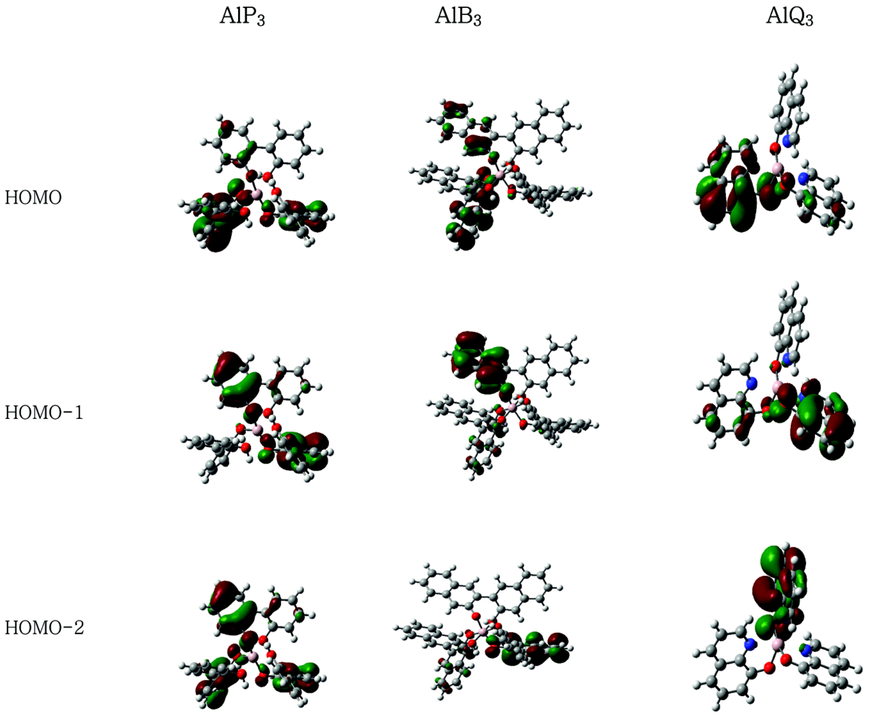


FIGURE 6 The highest occupied molecular orbital (HOMO) structure of Al (III) complexes.

Every gaps of newly proposed complexes are located in between AlP_3 and AlQ_3. Therefore, in the viewpoint of energy gap, newly designed complexes (AlP_3, AlB_3, AlC_3, and AlD_3) are good candidates for the blue emitting molecules.

HOMO and LUMO shapes of AlQ_3 largely preserve the electronic structures of Q ligand [16], but those of AlP_3 complex series are different from that of P ligand. For the case of HOMOs of AlP_3, the electron population are strongly localized on the linked phenol side. However, for the case of LUMOs, those are broadly spread on P ligand. Because the size of P ligand is bigger than Q ligand, P ligands in AlP_3 complex is affected steric hindrance by each other. Thus the molecular orbital structure of P ligand is different from that of P ligands in AlP_3.

The calculated absorption and emission wavelengths of AlP_3 complex and the experimental date of AlQ_3 and AlP_3 are summarized in Table 1. From the calculations of absorption and emission, it was resulted that the domainant transition of all Al(III) complexes is the one between HOMO and LUMO transition. Calculated emission wavelengths of new designed AlB_3, AlC_3 and AlD_3 are 357 nm, 377 nm and 364 nm, respectively, using TD-DFT(B1LYP/6-31G(d)) method. There is little difference between TD-DFT and CIS methods, as shown in Table 1. These results show the red shift, in comparison of AlP_3 complex, however it is still far from the 450 nm.

4. CONCLUSION

Al complexes were studied through computational methods. AlP_3 complex has higher intensity than that of AlQ_3, but its emission spectrum is out of visual region. We increase conjugation length to AlP_3 to shift emission spectrum to the longwave region. However emission spectra of newly designed molecules related to AlP_3 fail to reach to 450 nm. Further studies of these Al(III) complexes may lead to a new blue fluorescent of high luminescence efficiency.

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