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Density functional theory analysis of a mixed-ligand iridium compound for multi-color organic light-emitting diodes

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Electronic states and their energies are calculated for a mixed-ligand Ir(III) compound, (5-chloro-8-hydroxyquinoline) bis(2-phenylpyridyl) iridium (called IrQ(ppy)$_2$-5Cl) using time-dependent density functional theory (TDDFT) calculations and are compared with the experimental result. A good agreement is obtained between the calculated and measured absorption spectra. The d-π_Q^* molecular orbital transition gives the lowest-energy triplet state absorption band. Its energy is estimated as 1.84 eV (671 nm), which is close to the absorption band position of 1.86 eV (666 nm) observed for IrQ(ppy)$_2$-5Cl doped in 4,4′-*N*,*N*′-dicarbazole-biphenyl (CBP) host and of 1.88 eV (660 nm) observed for IrQ(ppy)$_2$-5Cl doped in polystyrene (PS). The second triplet state absorption band is caused by d-π_{ppy} transition. Its position is calculated as 2.51 eV (494 nm). The dipole moment is estimated as 3.45 D, which is lower than the dipole moment of *fac*-Ir(ppy)$_3$. This is understood by a reduced charge transfer between Ir(III) and quinoline ligand. Copyright © 2008 John Wiley & Sons, Ltd.

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INTRODUCTION

Organic light-emitting diodes (OLEDs) have been studied for high efficient OLED devices since Tang *et al.*[1] observed the first efficient electroluminescence from a two-layer organic device in 1987. Not only fluorescent organic molecules such as tris(8-hydrixyquinoline) aluminum (Alq$_3$) but also phosphorescent molecules such as *fac*-tris(2-phenylpyridine) iridium (Ir(ppy)$_3$) have been used as emitting materials.[2–4] An organic molecule gives luminescence with a unique color. For example, Ir(ppy)$_3$ gives green emission at 514 nm, while platinum octaethylporphyrin (PtOEP) gives red emission at 650 nm. To obtain white color emission, we have to mix various compounds of different color emissions in same host material. This leads to aggregation, phase separation, and different retardation among the different dopants. One way to avoid such a disadvantage is to use mixed-ligand compounds which give multi-color emission by discrete intramolecular transitions.[5,6]

As one of the mixed-ligand organometallic compounds, we recently prepared an Ir(III) compound, (5-chloro-8-hydroxyquinoline)bis(2-phenylpyridyl) iridium (IrQ(ppy)$_2$-5Cl).[7] This compound consists of two 2-phenylpyridine (ppy) ligands and one 8-hydroxyquinoline (Q) ligand, where one of the H atom in the Q ligand is substituted by a Cl atom. We obtained not only red phosphorescence due to the 8-hydroxyquinoline ligand but green phosphorescence due to ppy ligand.[7]

It is of great importance for both OLED scientists and engineers to be able to predict the solid-state electronic properties using a theoretical calculation, especially the information on the excited states of organometallic compounds. These approaches have been obtained using the time-dependent density functional theory (TDDFT).[8–10]

In this paper we calculate the electronic states and absorption spectra of IrQ(ppy)$_2$-5Cl compound using the TDDFT and compare the calculated results with the experimental results of absorption and photoluminescence.

CALCULATION AND EXPERIMENTAL METHODS

Molecular geometry of IrQ(ppy)$_2$-5Cl was optimized using Kohn-Sharm DFT.[11] The TDDFT calculation was made with Gaussian 03W software. We used the B3LYP hybrid exchange correlation functionals[12] and the Los Alamos National Laboratory double-polarized functions (LANL2DZ) as the basic sets because a better result was obtained by the B3LYP method than the classical Hartree-Fock method.[9] In the latter case the occupied d orbitals lies at lower energies compared with B3LYP

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functionals even if the d orbitals are less stables and more easily ionized in photoelectron spectra. An effective core potential (ECP) was used for Ir atom which has been used for $Ir(ppy)_3$.[9] Absorption spectra were derived as the spectra of oscillator strength *f*:

$$I(\lambda) = \sum_i f_i * \exp\left[-\left(\frac{\lambda - \lambda_i \max}{\Delta}\right)^2\right]$$

To obtain the spectrum, which consists of absorption bands, we assumed that each band has a Gaussian line shape with a half width of 15 nm. Molecular orbital contributions in each transition were calculated using the same method as developed by Gorelsky.[13] Calculation was also made for $Ir(ppy)_3$.

Mixed-ligand Ir-compound meridional-type $IrQ(ppy)_2$-5Cl was synthesized by the reaction of substituted 8-hydroxyquinoline with the diiridium complex tetrakis(2-phenylpyridyl)-μ-(dichloro) diiridium ($(C\wedge N)_2Ir$-μ-Cl_2) using the same method used previously.[7,14–16] Thin films of 5 wt% $IrQ(ppy)_2$-5Cl doped in 4,4′-*N*,*N*′-dicarbazole-biphenyl (CBP) and polystyrene (PS) were prepared by spin-coating the CH_2Cl_2 solutions on optical glass and quartz substrates under ambient atmospheric conditions. The spin-coating was made at a speed of 1000 and 3000 rpm for $IrQ(ppy)_2$-5Cl:CBP and $IrQ(ppy)_2$-5Cl:PS, respectively. The duration of spin-coating was 20 s. The films on quartz were used for absorption measurement. The films were not sealed in vacuum but aerated.

Absorption spectra were measured with a Shimadzu UV-3100 spectrophotometer. Photoluminescence spectra were measured at room temperature with a Spex Fluorolog-3 spectrophotometer. The excitation source was a 450 W Xe-lamp. Filters were used to avoid the half and second harmonics of the exciting light and luminescence.

EXPERIMENTAL RESULTS

Figure 1 shows the absorption and excitation spectra of IrQ(ppy)-5Cl neat film at room temperature. The excitation spectrum was obtained for 660 nm photoluminescence. The excitation spectrum agrees with the absorption spectrum, indicating the energy transfer from all the high-energy levels. Intense absorption band is observed at about 285 nm, and several weak absorption bands are observed at the low energy side, which extends to about 500 nm. The low-energy tail extends up to 700 nm, but the intensity of absorption band at 500–700 nm is too weak to be observed by the usual absorption measurement.

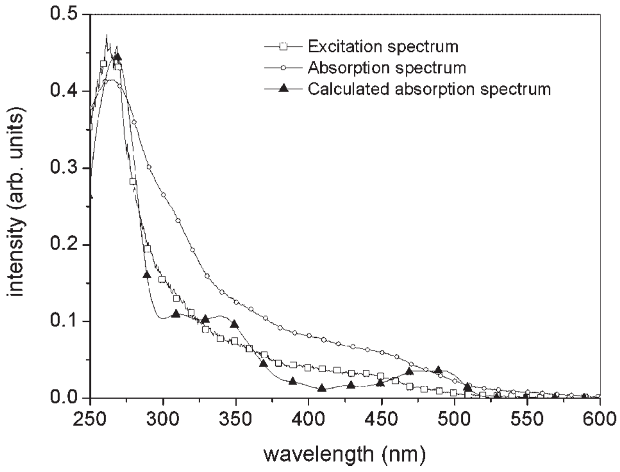


Figure 1. Measured and calculated absorption spectra of a $IrQ(ppy)_2$-5Cl neat film, together with excitation spectrum for 660 nm photoluminescence

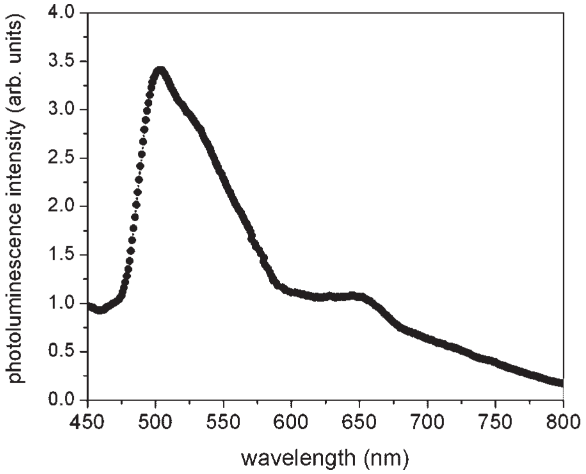


Figure 2. Emission spectrum of $IrQ(ppy)_2$-5Cl doped in polystyrene excited at 285 nm at room temperature

Photoluminescence spectrum of $IrQ(ppy)_2$-5Cl doped in PS is shown in Fig. 2. The excitation was made at 285 nm. An intense band with peak at about 503 nm and shoulder at about 525 nm is observed, which is similar to the emission band of $Ir(ppy)_3$.[17,18] Additionally a weak emission band is observed at about 658 nm. Similar emission band was observed at 666 nm in a film of $IrQ(ppy)_2$-5Cl doped in CBP.[7] Alq_3 gives also a broad phosphorescence at 660 nm.[19,20] Therefore, taking into account that red emission band with peak at 660 nm has been observed in Irq_3,[21,22] it is suggested to assign this red emission band to the triplet state of quinoline coupled with iridium.

CALCULATION RESULTS AND DISCUSSION

Bond length and molecular orbitals

The optimized bond lengths in $IrQ(ppy)_2$-5Cl molecule, which are calculated with the Gaussian 03 software, are summarized in Table 1. The calculated lengths from Ir atom to O (and also C, N of ppy and quinoline molecules) atom are compared with those

Table 1. Comparison of the calculated bond lengths for $IrQ(ppy)_2$-5Cl compared with the lengths estimated from X-ray diffraction measurement

	Calculated	X-ray diffraction
R (Ir–O), Å	2.188	2.146
R ($Ir–N_{ppy}$), Å	2.065	2.036
R ($Ir–N_{ppy}$), Å	2.050	2.037
R ($Ir–N_{Q}$), Å	2.177	2.128
R (Ir–C), Å	2.025	1.997
R (Ir–C), Å	2.017	1.995

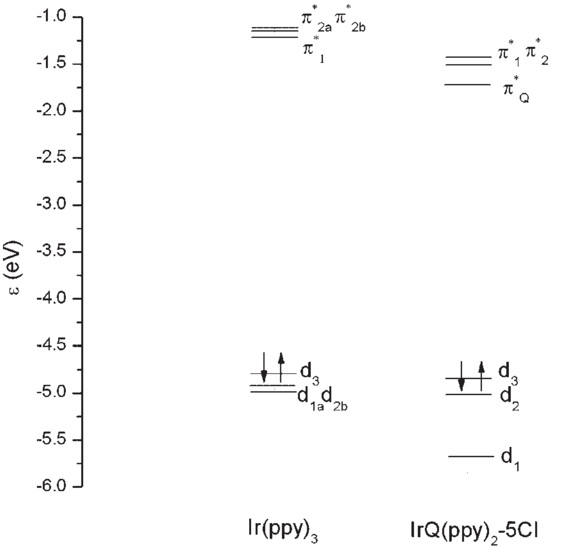


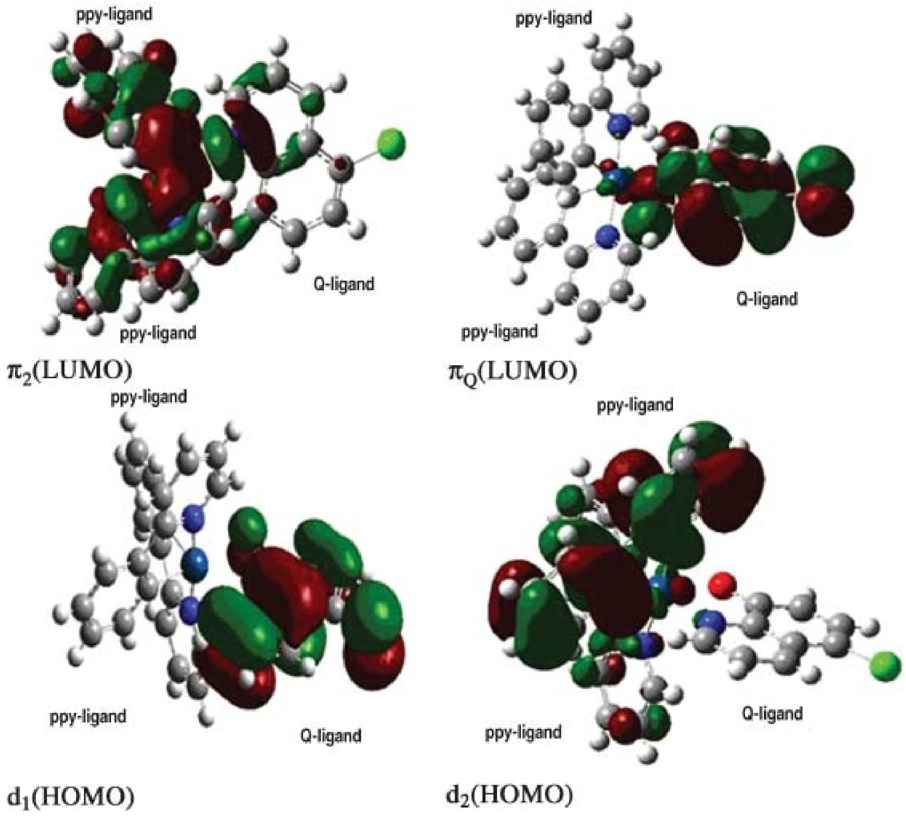
Figure 3. The HOMO and LUMO energies of IrQ(ppy)$_2$-5Cl and Ir(ppy)$_3$

obtained from X-ray diffraction.[7] A good agreement is obtained between the calculated and measured lengths although a small difference is found. IrQ(ppy)$_2$-5Cl has two ppy ligands. The optimized Ir—C bond length is slightly different between the two ppy ligands, that is, 2.025 Å and 2.017 Å. They are longer by about 0.025 Å than the experimental values. In the case of Ir—O bond, the calculated value is 2.188 Å, which is longer by 0.042 Å than the X-ray value. The same is true for the length of Ir and N of quinoline. Similar results were obtained for a mixed-ligand Ir-compound Ir(ppy)$_2$(acac),[9] that is, the lengths of Ir—O and Ir—N of acac ligand are longer by 0.03 and 0.05 Å than the values obtained by X-ray diffraction, respectively.

Regarding the angle between ligands, angle of 88.53° was obtained between quinoline and one ppy of two ppy ligands, 89.12° between quinoline and another ppy, and 95.15° between the two ppy ligands.

In the Ir-organometallic compounds, the highest occupied molecular orbital (HOMO) states are described using three 5d orbitals of Ir (d_{xz}, $d_{y2\text{-}z2}$, and d_{xy}, in order of increasing energy, named d_1, d_2, and d_3, respectively) The other two 5d orbitals are responsible for σ-bonding with the ligands. On the other hand, the lowest unoccupied molecular orbital (LUMO) states are mainly described using π orbitals of ligands. The calculated HOMO and LUMO energies of IrQ(ppy)$_2$-5Cl and Ir(ppy)$_3$ are shown in the Fig. 3. The results of Ir(ppy)$_3$ were obtained from Reference [9]. A difference is found for the HOMO states between Ir(ppy)$_3$ and IrQ(ppy)$_2$-5Cl. This difference is caused by weakly π-bonding ability of the O atom in quinoline ligand compared to the ppy ligand.

Figure 4 shows the counter plot of two HOMO (d_1 and d_2) and two LUMO orbitals (π_Q and π_{ppy}) of IrQ(ppy)$_2$-5Cl. The electron population analysis of each orbital shows a weak delocalization on the quinoline ligand and a strong delocalization on the ppy ligands. For Ir(ppy)$_3$, the resultant 5d character is 52% for d_1, 44% for d_2 and d_3, the lowest three LUMO states are combinations of the π^* orbital of ppy 9. On the other hand, for IrQ(ppy)$_2$-5Cl, the resultant 5d character is 76% for d_1, 63% for d_2, and 61% for d_3. The 5d character is much stronger for IrQ(ppy)$_2$-5Cl than for



π_2(LUMO)

π_Q(LUMO)

d_1(HOMO)

d_2(HOMO)

Figure 4. Counter plots some HOMO and LUMO orbitals of IrQ(ppy)$_2$-5Cl.

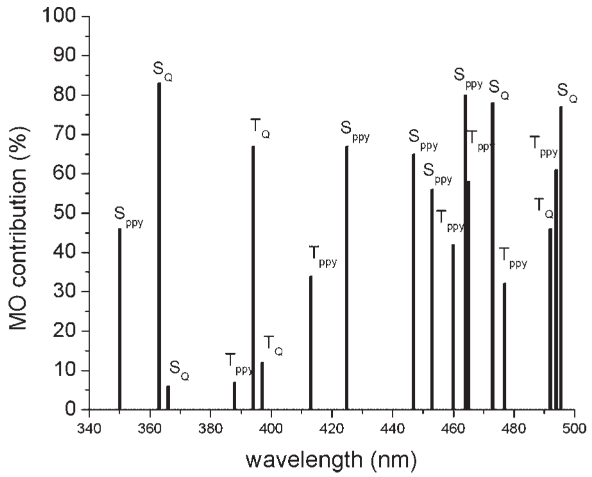


Figure 5. Molecular orbital (MO) contributions at the absorption spectrum (S, singlet; T, triplet). Line at 671 nm is not shown

Ir(ppy)$_3$. As seen in Fig. 4, the HOMO d$_1$ is delocalized over the quinoline ligand, while HOMO d$_2$ is delocalized over one of the two ppy ligands. Regarding the LUMO states, the π_2 is delocalized over the two ppy ligands, and π_Q is delocalized over the quinoline ligand.

Figure 5 shows the main molecular orbital contribution in each transition, that is, how many percentages the singlet and triplet transitions contributes to an absorption band. The percentage was obtained from the ratios between the coefficients of the wavefunctions responsible for the transitions. In this figure, only d-π^* transitions were plotted and π-π^* transitions are removed to show that the metal-ligand charge transfer (MLCT) transitions are predominantly responsible for the observed absorption spectra. The contribution of π-d transitions was negligible for the observed absorption spectra in the visible to ultraviolet (about 230 nm) range. The contributions of π-π^* appears in the computed spectrum of IrQ(ppy)$_2$-5Cl (Fig. 1).

Table 2 summarizes the calculated excitation energies and oscillator strength. According to this table, the lowest-energy band appears at 1.85 eV (corresponding wavelength is 670 nm). This band is caused by the electronic transition to the triplet state due to d$_3$-π_Q transition. The second triplet appears at 2.51 eV (494 nm), which is due to the d-π_1(i.e. π_{ppy}) transition. This absorption energy is close to the 2.55 eV (486 nm) absorption band energy measured for Ir(ppy)$_3$ neat film[17] and the 2.52 eV (492 nm) band energy observed by electroabsorption of Ir(ppy)$_3$.[23] The simultaneous observation of both the emissions at 503 nm and 658 nm (Fig. 2) may be attributed to the slow rate of electron transfer between π_Q and π_1 in the excited state.

The Gaussian 03W software for TDDFT calculation does not include the spin-orbit coupling effects and the results do not provide information about triplet–singlet absorption intensities. Spin-orbit coupling can mix the singlet and triplet states, therefore all the triplet states can contribute to the intensities in both absorption and emission states. However, the triplet states give zero oscillator strength in our calculation as made by Hay.[9]

The lowest-energy singlet state due to d-π_1(i.e. π_{ppy}) transition was calculated at 2.67 eV (Table 2). This state is lower by 0.13 eV than the corresponding state (2.8 eV) in Ir(ppy)$_3$.[9] Such a red shift is observed in the other mixed-ligand Ir-compounds where, like the case of IrQ(ppy)$_2$-5Cl, one of three ppy ligands in Ir(ppy)$_3$ is substituted with another ligand. For example, the first singlet of d-π_{ppy} contribution was found at 2.71 eV in Ir(ppy)$_2$(bza) and at 2.73 eV in Ir(ppy)$_2$(acac).[9]

Dipole moment

The orientation of dipole moment is shown in Fig. 6. The dipole moment tilts toward ppy ligand. The dipole moment of IrQ(ppy)$_2$-5Cl was estimated as 3.45 D, which is much smaller than the calculated dipole moment 6.4 D of Ir(ppy)$_3$. Our 6.4 D value is consistent with previously reported dipole moments for Ir(ppy)$_3$, that is, 6.14 D[24] and 6.26 D.[25]

Decrease of dipole moment has been shown for another mixed-ligand Ir-compound Ir(ppy)$_2$(acac), where one of the ppy ligands is substituted by another molecule acac. According to the TDDFT calculation by Park *et al.*,[25] the dipole moment also decreases from 6.26 D (Ir(ppy)$_3$) to 1.91 D (Ir(ppy)$_2$(acac)). In the following paragraphs, we consider the reason why the mixed ligand Ir-compounds show smaller dipole moment than Ir(ppy)$_3$.

The electron transfer gives rise to change of not only charge distribution in ligand but also charge on Ir. In fact, d character in the d$_1$ orbital is changed from 52% to 66–67%[9] and to 76% when molecule is changed from Ir(ppy)$_3$ to Ir(ppy)$_2$ (acac) and to

Table 2. Calculated excitation energies *E* (eV), dominant orbital excitation and oscillator strength *f* from TD-DFT calculation of IrQ(ppy)$_3$-5Cl

Triplet state	Excitation	*E* (eV)	Singlet state	Excitation	*E* (eV)	*f*
T_1	$d_3 \rightarrow \pi_Q^*$	1.85	S_1	$d_3 \rightarrow \pi_Q^*$	2.50	0.0398
T_2	$d_2 \rightarrow \pi_1^*$	2.51	S_2	$d_2 \rightarrow \pi_Q^*$	2.62	0.0318
T_3	$d_2 \rightarrow \pi_Q^*$	2.52	S_3	$d_3 \rightarrow \pi_1^*$	2.67	0.0109
T_4	$d_3 \rightarrow \pi_2^*$	2.60	S_4	$d_3 \rightarrow \pi_2^*$	2.73	0.0022
T_5	$d_3 \rightarrow \pi_1^*$	2.66	S_5	$d_2 \rightarrow \pi_1^*$	2.77	0.0153
T_6	$d_2 \rightarrow \pi_2^*$	2.69	S_6	$d_2 \rightarrow \pi_2^*$	2.92	0.0185
T_7	$d_1 \rightarrow \pi_1^*$	3.00	S_7	$d_1 \rightarrow \pi_Q^*$	3.39	0.0027
T_8	$d_1 \rightarrow \pi_Q^*$	3.12	S_8	$d_1 \rightarrow \pi_Q^*$	3.42	0.0439
T_9	$d_1 \rightarrow \pi_Q^*$	3.15	S_9	$d_1 \rightarrow \pi_1^*$	3.55	0.0352
T_{10}	$d_1 \rightarrow \pi_2^*$	3.20	S_{10}	$d_1 \rightarrow \pi_2^*$	3.55	0.0352

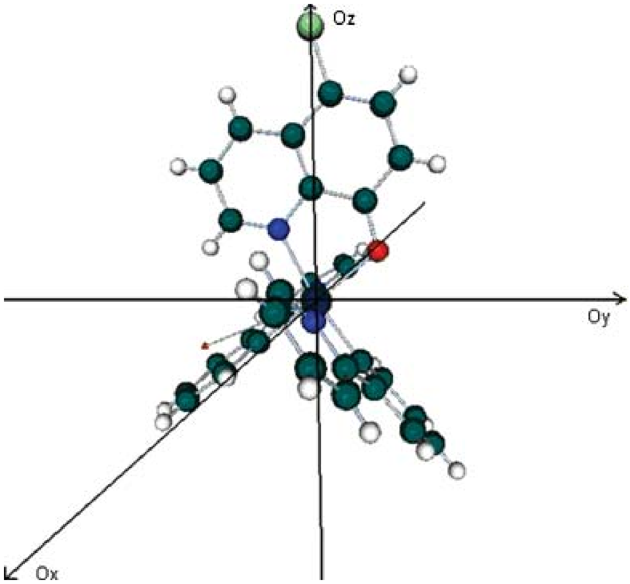


Figure 6. Orientation of dipole moment.

IrQ(ppy)$_2$-5Cl. From this result, it is suggested that electron transfer is responsible for the decrease of dipole moment in the mixed-ligand Ir-compounds.The fluctuating HOMO–LUMO gap is a key parameter in the Marcus model.[26] The HOMO–LUMO gap is relevant for the electron transfer reactions since the gap energy equals to ΔG of the Marcus equation. The gap energy becomes smaller in IrQ(ppy)$_2$-5Cl than in Ir(ppy)$_3$ as shown in Fig. 3. It is suggested that such a change gives rise to increase the 5d character from 52% (Ir(ppy)$_3$) to 76% (IrQ(ppy)$_2$-5Cl).

The λ and H_{AB} terms of the Marcus equation corresponds to the geometrical difference between the ground and excited states.[26] The two emission bands at about 503 nm and 658 nm are observed simultaneously in IrQ(ppy)$_2$-5Cl as shown in Fig. 2. The orthogonal arrangement between the quinoline and ppy ligands renders to a small value for the electronic coupling matrix H_{AB}, making such a double emission possible.

Absorption spectra

The TDDFT calculation gives the first spin-triplet state due to the Ir-quinoline ligand at 1.85 eV (670 nm). Unlike the cases of spin-singlet absorption bands, however, the present calculation does not give the information of its intensity because the Gaussian 03W software does not contain the spin-orbit interaction. The presence of 1.85 eV (670 nm) band is consistent with the appearance of 660 nm emission of IrQ(ppy)$_2$-5Cl. This indicates that the 660 nm emission is caused by the triplet state due to the d-π_Q transition in Ir-quinoline.

Using the oscillator strengths of Table 2, we obtain the calculated absorption spectrum of IrQ(ppy)$_2$-5Cl. The calculated spectrum (exactly speaking, the oscillator strength spectra) is shown in Fig. 1, where it is compared with the observed absorption spectrum of IrQ(ppy)$_2$-5Cl neat film. The high-energy calculated spectrum at 3.5–5.0 eV was obtained from the ligand-centered (LC) transitions. Absorption peaks appear at 494, 474, 427, 390, 359, 342, 309, and 267 nm in the calculated spectrum. These peaks almost agree with the observed absorption bands. The calculated spectrum is not inconsistent with the observed spectrum. For all the transitions including the d-π^* and π-π^* transitions in 250–350 nm region, calculation was made only for the singlet states, while, for the transition in 350–700 nm region, calculation was made both singlet and triplet states.

The present calculation was undertaken for a single molecule of IrQ(ppy)$_2$-5Cl, neglecting the intermolecular interaction and periodicity. The calculated result of absorption spectrum is close to the experimental results. The experiments of absorption and photoluminescence were done for the IrQ(ppy)$_2$-5Cl neat film and for films of PS and CBP doped with 5 wt% IrQ(ppy)$_2$-5Cl. All the IrQ(ppy)$_2$-5Cl molecules are randomly distributed in the doped film and even in the neat film, that is, the molecules are in the amorphous state and not in the crystalline state. This is confirmed from the experimental results that the absorption and photoluminescence spectra of IrQ(ppy)$_2$-5Cl are not different between the neat and doped films, and also from the results those spectra are quite similar to those of IrQ(ppy)$_2$-5Cl diluted in solutions such as cyclohexane and tetrahydrofuran.[27] Therefore it is suggested that a single-molecule (or free molecule) model is effective for not only the doped film but also for the neat film.

Recently Car-Parrinello molecular dynamics was applied to a hydrogen-bonded system in order to investigate the vibrational spectrum associated with O—H stretching.[28] We applied this theory to free IrQ(ppy)$_2$-5Cl molecule. A preliminary result shows only small difference in the Raman spectrum between the calculation and experiment. Influence of outer atoms in quinoline or pyridine is not significant. For example, change in the position of chlorine in IrQ(ppy)$_2$-5Cl does not give rise to the absorption spectra, which is confirmed by the experimental spectra.[27]

SUMMARY

The TDDFT calculation provides a good agreement with the observed absorption spectrum of IrQ(ppy)$_2$-5Cl. The HOMO states consist of 5d orbitals of Ir metal atom, while LUMO states consist of the ppy and quinoline ligand orbitals. The metal-to-ligand charge transfer (MLCT) to the ppy and quinoline ligands give rise to absorption bands in the visible-ultraviolet region. The quinoline ligand is responsible for the red emission observed at 666 nm for IrQ(ppy)$_2$-5Cl doped in CBP and at 660 nm for IrQ(ppy)$_2$-5Cl doped in PS because the TDDFT calculation suggests the absorption band due to the d_3-π_Q^* transition at 1.85 eV (670 nm).

The absorption band due to the transition to the lowest-energy triplet is calculated at 2.51 eV. This transition is made MLCT to the ppy ligand. The 2.51 eV band is close to the absorption band observed at 2.55 eV in neat film of Ir(ppy)$_3$ and also at about 2.48 eV in IrQ(ppy)$_2$-5Cl. Therefore the 2.48 eV absorption band of IrQ(ppy)$_2$-5Cl is attributable to triplet ^{3}MLCT transition. As a result, the green emission at 503 nm of IrQ(ppy)$_2$-5Cl is attributed to the ^{3}MLCT transition to the ppy ligand. Like this, the origins of dual emission (green and red photoluminescence) are clarified.

The intense high-energy absorptions due to the d_1-π_{ppy}^* and d_1-π_Q^* transition is expected to appear at 3.55 eV and 3.42 eV from the TDDFT calculation. Absorption bands observed at these spectral range in the neat film of IrQ(ppy)$_2$-5Cl are attributed to the singlet ^{1}MLCT transitions.

The dipole moment is estimated as 3.45 D. Such a small value is explained by the d-electron delocalization to ligands. Change of one ligand reduces the polarization of the molecule.

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