Visualization of Metal-to-Ligand and Ligand-to-Ligand Charge Transfer in Metal-Ligand Complexes

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Three methods including the atomic resolved density of state, charge difference density, and the transition density matrix are used to visualize metal to ligand charge transfer (MLCT) in ruthenium(II) ammine complex. The atomic resolved density of state shows that there is density of Ru on the HOMOs. All the density is localized on the ammine, which reveals that the excited electrons in the Ru complex are delocalized over the ammine ligand. The charge difference density shows that all the holes are localized on the Ru and the electrons on the ammine. The localization explains the MLCT on excitation. The transition density matrix shows that there is electron-hole coherence between Ru and ammine. These methods are also used to examine the MLCT in Os(bpy)\textsubscript{2}(p0p)Cl ("Os0p"; bpy=2,2’-bipyridyl; p0p=4,4’-bipyridyl) and the ligand-to-ligand charge transfer (LLCT) in Alq\textsubscript{3}. The calculated results show that these methods are powerful to examine MLCT and LLCT in the metal-ligand system.

Key words: Visualization, Metal to ligand, Ligand-to-ligand, Charge transfer

I. INTRODUCTION

Metal polypyridyl complexes, particularly those of ruthenium, lanthanide, and osmium, have long served as convenient templates for the study of the photoinduced properties of transition metal complexes [1-3]. The metal-to-ligand charge transfer (MLCT) transition that initiates much of the excited state processes exhibited by these compounds can be written as:

\[
[M^{II}(L)_3]^{2+} \overset{h\nu}{\longrightarrow} [M^{III}(L)(L^-)_{2}]^{2+}\quad (1)
\]

where photon absorption formally oxidizes the metal center and reduces the ligand [4]. Many experimental and theoretical works have been done to study the non-linear optical (NLO) response and the dynamics of MLCT for transition metal complexes [5-13].

Tris-(8-hydroxyquinolate)-aluminum (Alq\textsubscript{3}) is the key electroluminescent material currently used in organic light emitting devices (OLEDs) [14-17]. Alq\textsubscript{3} is a chelate compound with an Al ion surrounded by three 8-hydroxyquinoline ligands (Fig.1). The ligands are primarily responsible for the absorption of light and luminescence [15], which can be written as

\[
[M^{II}(L)_3]^{2+} \overset{h\nu}{\longrightarrow} [M^{II}(L^+)_{2}(L^-)]^{2+}\quad (2)
\]

Numerous studies have been carried out to examine the properties of Alq\textsubscript{3} directly related to its role in OLED devices; including the band structure of Alq\textsubscript{3},

FIG. 1 The chemical structure of the Ru(II) ammine complex where the atoms are labeled, Os(bpy)\textsubscript{2}(p0p)Cl, and Alq\textsubscript{3}.
TABLE I The calculated transition energies (TE), oscillator strengths (OS) of Ru(II) ammine complex, and CI coefficients (CIC) for the orbital transition from HOMOs to LUMOs.

<table>
<thead>
<tr>
<th></th>
<th>B3P86</th>
<th></th>
<th>B3LYP</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>TE/eV</td>
<td>TE/nm</td>
<td>OS</td>
</tr>
<tr>
<td>S1</td>
<td>2.2014</td>
<td>563.21</td>
<td>0.0000</td>
</tr>
<tr>
<td>S2</td>
<td>2.2319</td>
<td>555.50</td>
<td>0.0000</td>
</tr>
<tr>
<td>S3</td>
<td>2.5659</td>
<td>483.20</td>
<td>0.3283</td>
</tr>
</tbody>
</table>

the nature of the chemical bonding between metal and Alq$_3$, the mechanism of charge transport, and the nature of the excited electronic states giving rise to device emission [18-26]. The occupied electron states of Alq$_3$ have been investigated with soft X-ray photoelectron (SXRP) spectroscopy measurements, and the unoccupied states were probed with near-edge X-ray absorption (NEXRA) fine structure [27], and the optical physical properties of Alq$_3$ have been investigated with absorption spectrum and fluorescence spectrum [28-30].

In this work, three methods were used to visualize directly the MLCT on the optical excitation of the Ru(II) ammine complex [5,6] and Os(bpy)$_2$(p0p)Cl (“Osp0p”; bpy=2,2′-bipyridyl; p0p=4,4′-bipyridyl) [12] (Fig.1(b)). These methods are the atomic resolved density of state (DOS), charge difference density and the transition density matrix [31-36], respectively. The electronic structures and optical physical properties of Alq$_3$ were also studied theoretically with atom-resolved SXRP, NEXRA, absorption and fluorescence spectra, and the LLCT in absorption and fluorescence were explained theoretically.

II. METHODS

The geometry optimization of Ru(II) ammine complex and Os(bpy)$_2$(p0p)Cl were performed in the gas phase using the density functional theory (DFT) [37] with Becke’s three-parameter hybrid exchange functional with Lee-Yang-Parr gradient-corrected correlation functional (B3LYP functional) [38] and the LanL2DZ basis set [39]. Electronic transitions were calculated by time-dependent DFT (TD-DFT) [40] with B3LYP functional and the LanL2DZ basis set. For the comparison of the functionals, the excited state properties of Ru(II) ammine complex were also calculated with TD-B3P86 [41]/LanL2DZ/DFT-B3P86/LanL2DZ.

The ground state geometry optimization of Alq$_3$ was performed using DFT with B3LYP functional at the 3-21G basis level. The molecular geometry of the lowest excited states was optimized at the configuration interaction singles (CIS)/3-21G level [42]. The excited-state electronic structures were calculated using TD-DFT with B3LYP/3-21G method. At the excited-state optimal geometry, the transition frequency and oscillator strength correspond to the vertical fluorescence. Absorption and fluorescence points were treated at the TD-B3LYP/3-21G/B3LYP/3-21G and TD-B3LYP/3-21G/CIS/3-21G levels in conventional quantum-chemical notation “single point/optimization level”, respectively.

All theoretical calculations were carried out by the Gaussian 03 program [43]. The atomic resolved DOS were investigated with GaussSum [44]. The MLCT and LLCT were also studied with charge difference density and the transition density matrix.

III. RESULTS AND DISCUSSION

A. MLCT in Ru(II) ammine complex

The calculated transition energies (TE), oscillator strength (OS) of Ru(II) ammine complex and CI coefficients (CIC) for the orbital transitions from HOMOs and LUMOs of the first three lowest singlet excited states are listed in Table I. The results are consistent with the theoretical calculations by Coe et al. [6]. The calculated results show that influence of the functionals, both B3LYP and B3P86, on the transition energies is small. The DOS of Ru(II) and ammine complex shows that all the density is localized on the Ru(II) for HOMO-2, HOMO-1 and HOMO; while all the density is localized on the ammine for the LUMO (Fig.2), which clearly reveals that the excited electron in the Ru is delocalized over the ammines ligand during absorption, which is direct evidence of MLCT on the charge transfer absorption transition.

The second evidence of MLCT can be seen from the charge difference density (Fig.3). All the holes are local-
TABLE II The calculated transition energies (TE), oscillator strengths (OS) and CI coefficients for the orbital transition from HOMOs to LUMOs in absorption of Os(bpy)$_2$(p0p)Cl.

<table>
<thead>
<tr>
<th></th>
<th>TE</th>
<th>f</th>
<th>CI coefficients</th>
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</thead>
<tbody>
<tr>
<td>S1</td>
<td>1.7365</td>
<td>0.0098</td>
<td>-0.22 (H-2→L), 0.63 (H→L)</td>
</tr>
<tr>
<td>S2</td>
<td>1.8737</td>
<td>0.0022</td>
<td>-0.18 (H-1→L), 0.66(H→L+1)</td>
</tr>
<tr>
<td>S3</td>
<td>1.9307</td>
<td>0.0010</td>
<td>0.65(H-1→L), 0.19 (H→L+1)</td>
</tr>
<tr>
<td>S4</td>
<td>2.3057</td>
<td>0.0043</td>
<td>-0.14(H-2→L), 0.63(H-2→L+1), -0.21(H-1→L+1)</td>
</tr>
<tr>
<td>S5</td>
<td>2.3439</td>
<td>0.0364</td>
<td>-0.34(H-2→L), 0.17(H-1→L+1), 0.18(H→L), 0.51(H→L+2), -0.15(H→L+3)</td>
</tr>
<tr>
<td>S6</td>
<td>2.3577</td>
<td>0.0595</td>
<td>0.43(H→L), -0.21(H-1→L+1), 0.46(H→L+2), -0.10(H→L+4)</td>
</tr>
<tr>
<td>S7</td>
<td>2.4539</td>
<td>0.0711</td>
<td>0.17(H-2→L), 0.26(H-2→L+1), 0.53(H-1→L+1), 0.11(H→L+3), -0.10(H→L+4), -0.18(H→L+6)</td>
</tr>
<tr>
<td>S8</td>
<td>2.6084</td>
<td>0.0058</td>
<td>-0.14(H-2→L), -0.12(H-1→L+3), 0.63(H→L+3), 0.18(H→L+4)</td>
</tr>
<tr>
<td>S9</td>
<td>2.6834</td>
<td>0.0222</td>
<td>0.69(H-1→L+2)</td>
</tr>
<tr>
<td>S10</td>
<td>2.8585</td>
<td>0.0070</td>
<td>0.61(H-1→L+3), 0.30(H-2→L+4)</td>
</tr>
</tbody>
</table>

FIG. 3 Charge difference density for the third excited state of Ru(II) ammine complex.

Table II shows the calculated transition energies, oscillator strengths, and CI coefficients for the orbital transition from HOMOs to LUMOs in absorption of Os(bpy)$_2$(p0p)Cl.

B. MLCT in Os(bpy)$_2$(p0p)Cl

The calculated TE, OS, and the CIC of the orbital transitions for the lowest ten singlet electronic states in absorption of Os(bpy)$_2$(p0p)Cl are listed in Table II. The simulated absorption spectrum shows the main absorption peak is around 500 nm with the absorption edge at 714 nm (see Fig.S1 in supplementary material). To study the electronic structure and the excited state properties of Os(bpy)$_2$(p0p)Cl, it is essential to analyze the atomic-resolved DOS of the HOMOs and LUMOs (see Fig.S2 in supplementary material). The electronic state transitions of the lowest ten singlet excited states are the MLCT states. MLCT are further investigated with charge difference densities (see Fig.S3 in supplementary material). Clearly, all of the states are the MLCT excited states, the excited electrons on Os and Cl transfer to one of ligands. Note that some densities are also localized on the Cl, so the Cl can also be an electron donor in the charge transfer. For the LUMOs, all the densities are localized on the ligands. To be specific, the densities are localized on one of the ligands for LUMO, LUMO+1 and LUMO+2. Therefore, according to the DOS of LUMOs, the ligands will be electron acceptors.

C. LLCT in Alq$_3$

The calculated transition energies and oscillator strengths of the lowest seven singlet excited states in
absorption are listed in Table III, and the calculated spectroscopy results (see Fig.S5 in supplementary material) are consistent with the experimental data [19]. Six molecular orbitals (HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1, and LUMO+2) are involved for these excited states in absorption, and these HOMOs and LUMOs constitute the first peak of SXRP and NEXRA spectra, respectively.

1. Electronic structures of Alq₃ studied with SXRP and NEXRA spectra

The SXRP of Alq₃ (Fig.S6(a) in supplementary material) reveals the energy levels of HOMOs and atom-resolved DOS. The calculated DOS is consistent with the experimental and Curonia’s theoretical data [18]. Compared to the experimental data [18], the calculated energy levels of HOMOs are blue shifted about 0.25 eV, so that the energy of the leading maximum matches that observed in the experiment, which is from the choice of the functional of DFT. It has been shown that the energy levels of HOMOs and LUMOs are heavily dependent on the kind of functional [35]. The contribution of Al to these occupied states is vanishingly small. The SXRP spectroscopy shows the first peak is divided into “triplet”, which has the same orbital character as that on each of the three ligands. Comparing the contribution of N and that of O to the first peak, there is only a weak contribution coming from O, which implies that oxidizing agents will attack the molecule at the phenoxide side of the ligands. The first three peaks of NEXRA spectrum are also grouped into “triplet”, and the most contributions of the DOS are from C (see Fig.S6(b) in supplementary material). The contribution of Al to these unoccupied states is also vanishingly small. The HOMO and LUMO results show there are the same orbital characteristics on LUMO+1 and LUMO+2 (the density is delocalized on two ligands), which are different from LUMO (the density is localized on one ligand)(Fig.S7 in supplementary material). Comparing the contribution of N and that of O to the first peak, there is only a weak contribution coming from N, which implies that the reducing agents will attack the molecule at the pyridyl side.

2. Excited state properties of Alq₃

It is very interesting to study the electron-hole coherence and intramolecular charge transfer for the transitions from the ground state to the excited states on the excitation. The contour plots of the transition density matrix (Fig.S8 in supplementary material) show that S₁, S₂, S₅, and S₇ are the intermolecular charge transfer (ICT) excited states, since the electron-holes...
are mainly cohered between two ligands. To show the orientation of ICT, the charge difference density is employed. The charge difference densities (Fig. S9 in supplementary material) shows the orientation of electron transfer on ligands. For S3, S4, and S6, the contour plots of transition density matrix reveal that they are the localized excited states, since electron-hole pairs are localized on one of ligands. Furthermore, from their charge difference densities, the orientation of localized ICT in the one ligand is from phenoxide side to pyridyl side, which supports the calculated DOS (where for the first peak of SXRP spectrum is mainly contributed from O, while for the first peak of NEXRA spectrum is mainly contributed from N). From the contour plot of transition density matrix and charge difference density in fluorescence, it is a localized excited state, and the electrons move back from the pyridyl side to phenoxide side.

IV. CONCLUSION

Visualizations of MLCT in Ru(II) ammine complex and Os(bpy)2(p0p)Cl were revealed and conformed by the atomic resolved density of state, the charge difference density, the transition density matrix and Raman spectroscopy. The calculated results of the atomic-resolved SXRP and NEXRA spectra, charge difference densities and transition density matrix clearly reveal that there is a LLCT in absorption and fluorescence of Alq3.

Supplementary materials: Supplementary materials are available at the CJCP website alongside the main article.

V. ACKNOWLEDGMENTS

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