A series of 4,5-diazafluoren-9-one-derived ligands and their Cu(I) complexes: Synthesis, characterization and photophysical properties

Liming Zhang a,b, Bin Li a,∗

a Key Laboratory of Excited State Processes, Changchun Institute of Optics Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, PR China
b Graduate School of the Chinese Academy of Sciences, Chinese Academy of Sciences, Beijing 100039, PR China

1. Introduction

The development of practical components for chemical sensors, display devices, probes of biological systems, and solar energy conversion schemes has sparked an interest in complexes of diimine ligands with transition metals, especially heavy metal ions such as ruthenium(II) and rhenium(I) [1–3]. At the same time, the strong appeal of using cheaper copper complexes to replace more expensive compounds based on noble metal ions and the need for a deeper understanding of correlation between structural processes and photophysical properties have led to continuous progress in the design of Cu(I) complexes [4,5].

Generally, emission signal from the charge-transfer (CT) excited state of Cu(I) complexes is typically weak and short-lived because the lowest-energy CT state of a d10 system involves excitation from a metal–ligand dπ* orbital. An important consequence is that the excited state typically prefers a tetragonally flattened geometry, whereas the ground state usually adopts a more tetrahedral-like coordination geometry that is appropriate for a closed-shell ion. Aside from reducing energy content, the geometry distortion that occurs in excited state facilitates relaxation back to ground state. Moreover, donor media also tend to quench the excited state. In this paper, 4,5-diazafluoren-9-one-derived ligands, incorporated with electron-donor or electron-acceptor moieties, and their corresponding [Cu(diimine ligand)(POP)]BF4 complexes are synthesized to explore relationships between diimine ligand electronic structure and photophysical properties of their corresponding Cu(I) complexes. It is found that the introduction of an electron-donor moiety into one diimine ligand leads to a dramatic red shift of the absorption of corresponding Cu(I) complex, while, an electron-acceptor moiety demonstrates no obvious effect on Cu(I) complex absorption when introduced into diimine ligand. In addition, it is found that the intraligand charge transfer of Dafo-derived ligands acts as an efficient luminescence quencher within their corresponding Cu(I) complexes, leading to luminescence absence from metal-to-ligand-charge-transfer (MLCT) excited state.

In this paper, a series of 4,5-diazafluoren-9-one-derived (Dafo-derived) diimine ligands and their corresponding Cu(I) complexes with bis(2-(diphenylphosphanyl)phenyl) ether as the auxiliary ligand are synthesized. Relationships between diimine ligands and photophysical properties of their corresponding Cu(I) complexes are discussed in detail. It is found that the introduction of an electron-donor moiety into one diimine ligand leads to a dramatic red shift of the absorption of corresponding Cu(I) complex, while, an electron-acceptor moiety demonstrates no obvious effect on Cu(I) complex absorption when introduced into diimine ligand. In addition, it is found that the intraligand charge transfer of Dafo-derived ligands acts as an efficient luminescence quencher within their corresponding Cu(I) complexes, leading to luminescence absence from metal-to-ligand-charge-transfer (MLCT) excited state.

Keywords: Cu(I) complexes Luminescence quenching Diimine ligand

A B S T R A C T

In this paper, a series of 4,5-diazafluoren-9-one-derived (Dafo-derived) diimine ligands and their corresponding Cu(I) complexes with bis(2-(diphenylphosphanyl)phenyl) ether as the auxiliary ligand are synthesized. Relationships between diimine ligands and photophysical properties of their corresponding Cu(I) complexes are discussed in detail. It is found that the introduction of an electron-donor moiety into one diimine ligand leads to a dramatic red shift of the absorption of corresponding Cu(I) complex, while, an electron-acceptor moiety demonstrates no obvious effect on Cu(I) complex absorption when introduced into diimine ligand. In addition, it is found that the intraligand charge transfer of Dafo-derived ligands acts as an efficient luminescence quencher within their corresponding Cu(I) complexes, leading to luminescence absence from metal-to-ligand-charge-transfer (MLCT) excited state.
5-diazfluoren-9-one-derived ligands acts as an efficient luminescence quencher within their corresponding Cu(I) complexes, leading to luminescence absence from MLCT excited state.

2. Experimental details

A scheme showing all the molecular structures studied in this paper is given as Scheme 1.

2.1. Synthesis of ligands

A typical synthetic procedure for Dafo-derived ligands (L1–L5) is given as follows. A mixture of 1 mmol of Dafo, 1.2 mmol of phenylamine (PA), 0.1 mmol of N,N-dimethyl-benzene-1,4-diamine (DMBDA) and 1,10-phenanthroline (phen) were purchased from Aldrich Chemical Co. and used without further purification.

2.2. Synthesis of Cu(I) complexes

All the Cu(I) complexes were synthesized following the literature procedure [8].

[Cu(L1)(POP)]BF₄: ¹H NMR (CDCl₃): δ 8.83 (s, 1H), 8.67 (s, 1H), 8.27 (s, 1H), 7.76–7.30 (m, 3H), 7.24–7.17 (m, 2H), 7.01–6.97 (m, 3H). ¹³P NMR δ +1.65 (s, P(C₆H₅)₂C₆H₄). Anal. Calc. for C₁₇H₁₄N₃O: C, 78.74; H, 5.05; N, 16.20. Found: C, 79.28; H, 4.98; N, 16.18.

[Cu(L2)(POP)]BF₄: ¹H NMR (CDCl₃): δ 8.29 (s, 1H), 8.66 (s, 1H), 8.24 (s, 1H), 7.38 (s, 1H), 7.29 (s, 5H), 7.16 (s, 6H), 7.10 (s, 1H), 7.05 (s, 2H), 6.95–6.90 (m, 2H). Anal. Calc. for C₁₉H₁₆N₄: C, 75.73; H, 5.48; N, 18.65. Found: C, 75.78; H, 5.37; N, 18.75.

[Cu(L3)(POP)]BF₄: ¹H NMR (CDCl₃): δ 8.31 (s, 1H), 7.37 (s, 2H), 7.03–6.98 (m, 3H), 6.81–6.79 (m, 2H), 3.03 (s, 6H). Anal. Calc. for C₁₇H₁₁N₃: C, 79.36; H, 4.31; N, 16.33. Found: C, 79.28; H, 4.45; N, 16.18.

[Cu(L4)(POP)]BF₄: ¹H NMR (CDCl₃): δ 8.79 (s, 1H), 8.65 (s, 1H), 8.21–8.11 (m, 4H), 7.56–7.43 (m, 4H), 7.15 (s, 2H), 6.86 (s, 2H), 2.67 (s, 3H). Anal. Calc. for C₁₉H₁₅N₄O: C, 75.78; H, 5.37; N, 18.75. Found: C, 75.31; H, 4.28; N, 16.73.

[Cu(L5)(POP)]BF₄: ¹H NMR (CDCl₃): δ 8.77 (s, 1H), 8.64 (s, 1H), 8.25 (s, 1H), 7.37 (s, 2H), 7.03–6.98 (m, 3H), 6.81–6.79 (m, 2H), 3.03 (s, 6H). Anal. Calc. for C₁₇H₁₅N₃: C, 78.65; H, 5.11; N, 16.11. Found: C, 78.69; H, 4.98; N, 16.18.

2.3. Characterization of Cu(I) complexes

The molecular structures of ligands and complexes are given as Scheme 1.

[Scheme 1. The molecular structures of ligands and complexes.]
Fig. 1. Absorption spectra of diimine ligands in CH₂Cl₂ with a concentration of 1 × 10⁻⁵ mol/L.

Table 1

<table>
<thead>
<tr>
<th>Bond length</th>
<th>Cal. a</th>
<th>Exp. b</th>
<th>Bond angle</th>
<th>Cal. a</th>
<th>Exp. b</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3–N4</td>
<td>1.378</td>
<td>1.344</td>
<td>C3–N4–C12</td>
<td>116.22</td>
<td>114.71</td>
</tr>
<tr>
<td>N4–C12</td>
<td>1.341</td>
<td>1.329</td>
<td>C6–N5–C13</td>
<td>116.31</td>
<td>114.14</td>
</tr>
<tr>
<td>C12–C13</td>
<td>1.492</td>
<td>1.486</td>
<td>N4–C12–C13</td>
<td>128.68</td>
<td>126.92</td>
</tr>
<tr>
<td>N5–C13</td>
<td>1.341</td>
<td>1.328</td>
<td>C12–C13–N5</td>
<td>128.48</td>
<td>125.30</td>
</tr>
<tr>
<td>N5–C6</td>
<td>1.369</td>
<td>1.349</td>
<td>C10–C12–C13</td>
<td>107.77</td>
<td>107.65</td>
</tr>
<tr>
<td>C9–C10</td>
<td>1.492</td>
<td>1.481</td>
<td>C11–C12–C13</td>
<td>107.89</td>
<td>108.65</td>
</tr>
<tr>
<td>C9–C11</td>
<td>1.496</td>
<td>1.491</td>
<td>C10–C9–C11</td>
<td>104.95</td>
<td>105.41</td>
</tr>
<tr>
<td>C9–N14</td>
<td>1.284</td>
<td>1.276</td>
<td>C11–C9–N14</td>
<td>132.66</td>
<td>132.73</td>
</tr>
<tr>
<td>N14–C15</td>
<td>1.430</td>
<td>1.414</td>
<td>C9–N14–C14</td>
<td>125.13</td>
<td>121.67</td>
</tr>
</tbody>
</table>

a Calculated at R3LYP/6-31G(d) level.  b Ref. [16].

of L1 shows a predominant π character of the introduced aniline moiety, while, LUMO of L1 is essentially π* of Dafo moiety. Considering Ln’s (n = 2, 3, 4, 5) similar molecular structures to that of L1, it is reasonable to expect that Ln’s HOMOs localize on the introduced electron-donor/acceptor moieties, while, LUMOs are π* of Dafo moiety. The introduction of electron-donor moieties into Dafo dramatically lifts molecular π, with π* largely unaffected, leading to the above mentioned absorption spectrum red shift of L4 and L5. While, no obvious spectral shift is observed for L2 and L3, compared with the absorption spectrum of L1, indicating that there is no obvious difference between aniline moiety π and that of oxadiazol-derived moieties.

3.2. Absorption of [Cu(Ln)(POP)]BF₄

UV–Vis spectra of [Cu(Ln)(POP)]BF₄ (n = 1, 2, 3, 4, 5) and POP in CH₂Cl₂ with a concentration of 1 × 10⁻⁵ mol/L are shown in Fig. 3, and their absorption peaks are summarized in Table 2. [Cu(Ln)(POP)]BF₄ (n = 1, 2, 3, 4, 5) exhibit similar low-energy band shapes to those of diimine ligands. The absorption band peaking at ~230 nm is assigned as the absorption overlap of LLCT and MLCT transitions according to the previous report (LLCT = ligand-to-ligand-charge-transfer) [10]. On the other hand, the lowest-energy absorption bands of [Cu(Ln)(POP)]BF₄ (n = 1, 2, 3) exhibit no obvious spectral shift compared with those of Ln (n = 1, 2, 3), suggesting that electronic effect of oxadiazol-derived moieties on absorption spectrum is small enough to be neglected. From the comparison between absorption spectra of L4, L5 and their corresponding Cu(I) complexes, we can say that although the lowest-energy bands of [Cu(L4)(POP)]BF₄ and [Cu(L5)(POP)]BF₄ are largely red shifted, it seems that they still belong to the intraligand tran-
tions of diimine ligands. While, the newly generated bands peaking at \( \lambda \approx 390 \) nm are assigned as MLCT absorptions. The role played by electron-donor moieties is clearly established when we come to an absorption spectra comparison between \([\text{Cu(L4/L5)(POP)}]_{\text{BF4}}\) and \([\text{Cu(L1)(POP)}]_{\text{BF4}}\). Even though their molecular structures are quite similar to each other, large scale absorption red shifts are observed for \([\text{Cu(L4/L5)(POP)}]_{\text{BF4}}\), which is caused by the increasing electron density in L4/L5. Thus, we come to a conclusion that the introduction of electron-donor moieties into diimine ligands leads to a red shift of absorption, on the other hand, electron-acceptor moieties exhibit no obvious effect on Cu(I) complexes absorption.

3.3. Electron-donor effect

The Cu(I) complexes of \([\text{Cu(Ln)(POP)}]_{\text{BF4}}\) \((n = 1, 2, 3, 4, 5)\) demonstrate no emission in solid state at both room temperature and low temperature (77 K). As we mentioned, the lowest-energy transition within the five Cu(I) complexes is an intramolecular one. Thus, the MLCT excited state radiative transition in Cu(I) complexes is largely suppressed by the intramolecular transition, leading to luminescence absence from MLCT excited state in \([\text{Cu(Ln)(POP)}]_{\text{BF4}}\) \((n = 1, 2, 3, 4, 5)\). In order to test this hypothesis, L6 and its corresponding Cu(I) complex are introduced. The lowest-energy transition of reference diimine ligand, L1, has been determined to be an intraligand one from aniline moiety to Dafo moiety. As for L6, the conjugation system is broken: aniline and Dafo moieties are connected by an inert spacer so that the intraligand transition can be stopped. Fig. 4 exhibits the UV–Vis absorption spectra of L6 and \([\text{Cu(L6)(POP)}]_{\text{BF4}}\) as well as the solid state photoluminescence spectra of \([\text{Cu(L6)(POP)}]_{\text{BF4}}\) upon excitation wavelength of 355 nm at room temperature. The emission from \([\text{Cu(L6)(POP)}]_{\text{BF4}}\) confirms that the radiative transition is indeed suppressed by the intramolecular transition as we suggested. In addition, absorption spectrum comparison between L6 and \([\text{Cu(L6)(POP)}]_{\text{BF4}}\) suggests that the newly generated absorption band peaking at 380 nm of \([\text{Cu(L6)(POP)}]_{\text{BF4}}\) should be MLCT transitions. Thus, the transition type of \([\text{Cu(Ln)(POP)}]_{\text{BF4}}\) \((n = 1, 2, 3, 4, 5)\) should be MLCT transition (near UV and purple region) plus intraligand transition (blue, green and red region).

4. Conclusion

In this paper, a series of diimine ligands and their corresponding Cu(I) complexes are synthesized. Relationships between diimine ligands and photophysical properties of their corresponding Cu(I)
complexes are discussed in detail. It is found that the introduction of electron-donor into diimine ligand leads to a dramatic red shift of the absorption of corresponding Cu(I) complex, while, electron-acceptor demonstrates no obvious effect on Cu(I) complex absorption when introduced into diimine ligand. In addition, it is found that intraligand charge transfer of Dafo-derived ligands acts as an efficient luminescence quencher within their corresponding Cu(I) complexes, leading to luminescence absence from MLCT excited state.

Acknowledgments

The authors gratefully thank the financial supports of One Hundred Talents Project from Chinese Academy of Sciences and the National Natural Science Foundations of China (Grant No. 50872130).

References