Inorg. Chem. **2003**, *42*, 3393–3395

Inorganic Chemistry
Communication

Dual Emission from ^{3}MLCT and ^{3}ILCT Excited States in a New Ru(II) Diimine Complex

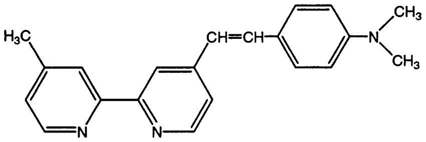
Lin-qing Song,[†] Juan Feng,[‡] Xue-song Wang,*,[†] Jun-hua Yu,[†] Yuan-jun Hou,[†] Pu-hui Xie,[†] Bao-wen Zhang,*,[†] Jun-feng Xiang,[‡] Xi-cheng Ai,[‡] and Jian-ping Zhang*,[‡]

Technical Institute of Physics and Chemistry, Chinese Academy of Sciences,
Beijing, 100101 P. R. China, and State Key Laboratory for Structural Chemistry of Unstable and
Stable Species, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100080 P. R. China

Received September 29, 2002

The unique behavior of a new Ru(II) diimine complex, Ru(bpy)$_2$(L)$^{2+}$ (where L is 4-methyl-4′-[*p*-(dimethyl- amino)-α-styryl]-2,2′-bipyridine, bpy is 2,2′-bipyridine), was studied in detail. Due to the strong electron donating property of the amino group, an ILCT (intraligand charge transfer) state is involved either in the absorption spectra or in the time-resolved emission spectra. Dual emission based on ^{3}MLCT and ^{3}ILCT states was observed at room temperature for the first time via a time-resolved technique in Ru(II) diimine complexes.

Chart 1



The photophysical properties of Ru(II) diimine complexes have been studied for decades due to their potential applications in luminescence sensing,[1,2] solar energy conversion,[3] etc. All of them exhibit metal-to-ligand charge transfer (MLCT) absorption bands in the UV−vis region, and in most cases, luminescence originates from the ^{3}MLCT states. As an additional approach for tuning excited-state energies in Ru(II) diimine complexes, coexistence of ^{3}MLCT with ^{3}IL (intraligand) or ^{3}ILCT (intraligand charge transfer) states was explored by many groups.[4−10] Among these complexes, pyrene is often introduced and linked to the diimine component through a variety of covalent linkages.[7−10] Although the ^{3}MLCT and ^{3}IL or ^{3}ILCT states can coexist, dual emission is generally not observed in these species. Recently, Castellano et al.[11] observed ^{3}IL and ^{3}MLCT luminescence simultaneously using time-resolved luminescence spectroscopy at 77 K in a Ru(II) diimine complex. In an effort to further explore the excited-state properties of Ru(II) diimine complexes, we have examined the behavior of a new complex, Ru(bpy)$_2$(L)(PF$_6$)$_2$ (where L is 4-methyl-4′-[*p*-(dimethylamino)-α-styryl]-2,2′-bipyridine, bpy is 2,2′-bipyridine). In the ligand L (Chart 1), the strong electron donating property of the substituent, *N*,*N*-dimethylaniline (DMA), makes it facile to form an ILCT (intraligand charge transfer) transition from the DMA moiety to the bipyridine moiety. As a result, two separate emission bands belonging to ^{3}MLCT and ^{3}ILCT states were observed at room temperature for the first time via a time-resolved technique. This work opens up another way to make ^{3}MLCT and ^{3}ILCT states coexist and provides a new model for studying the excited-state behavior of Ru(II) diimine complexes.

The free ligand L exhibits an absorption maximum at 380 nm in an ethanol solution. An ILCT transition is believed to be involved in this process. The strong electron donating property of the amino substituent in ligand L raises the energy level of the DMA group to such an extent that a DMA (π) to bipyridine (π*) charge-transfer transition exists with certainty. Some 4′-aryl-terpyridine ligands with amino substituents have been proven to possess ILCT transitions.[12,13]

---

* To whom correspondence should be addressed. E-mail: g203@ipc.ac.cn (B.-w.Z.).

[†] Technical Institute of Physics and Chemistry.

[‡] State Key Laboratory for Structural Chemistry of Unstable and Stable Species.

(1) de Silver, A. P.; Gunaratne, H. Q.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P. *Chem. Rev.* **1997**, *97*, 1515−1560.
(2) Beer, P. D. *Acc. Chem. Res.* **1998**, *31*, 71−80.
(3) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737−739.
(4) Shaw, J. R.; Webb, R. T.; Schmehl, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 1117−1123.
(5) Baba, A. I.; Ensley, H. E.; Schmehl, R. H. *Inorg. Chem.* **1995**, *34*, 1198−1207.
(6) Taffarel, E.; Chirayil, S.; Kim, W.; Thummel, R.; Schmehl, R. H. *Inorg. Chem.* **1996**, *35*, 2127−2131.
(7) Ford, W. E.; Rodgers, M. A. J. *J. Phys. Chem.* **1992**, *96*, 2917−2920.
(8) Wilson, G. J.; Sasse, W. H. F.; Mau, A. W. H. *Chem. Phys. Lett.* **1996**, *250*, 583−588.
(9) Harriman, A.; Hissler, M.; Khatyr, A.; Ziessel, R. *Chem. Commun.* **1999**, 735−736.
(10) Del Guerzo, A.; Leroy, S.; Fages, F.; Schmehl, R. H. *Inorg. Chem.* **2002**, *41*, 359−366.
(11) Tyson, D. S.; Luman, C. R.; Zhou, X.; Castellano, F. N. *Inorg. Chem.* **2001**, *40*, 4063−4071.
(12) Mutai, T.; Cheon, J. D.; Arita, S.; Araki, K. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1045−1050.
(13) Goodall, W.; Gareth Williams, J. A. *Chem. Commun.* **2001**, 2514−2515.

10.1021/ic026070j CCC: $25.00

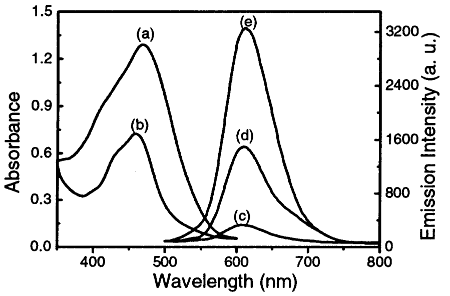


Figure 1. Electronic absorption spectra (left) of $Ru(bpy)_2(L)^{2+}$ (a) and $Ru(bpy)_2(L)^{2+} + H^+$ (b) and emission spectra (right) of the complex in aerated (c), deaerated (d), and H^+ containing (e) conditions in methanol at room temperature. For emission spectra, the excitation wavelength is 460 nm.

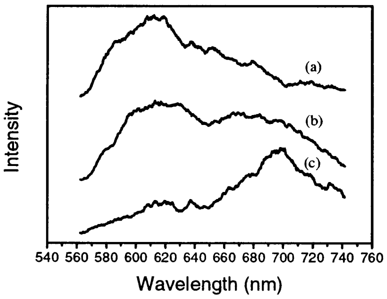


Figure 2. Time-resolved emission spectra ($\lambda_{exc} = 460$ nm) in EtOH/MeOH (4:1) solution at room temperature measured with the following delay/gate width settings: (a) 0.66 μs/100 ns; (b) 1.6 μs/300 ns; and (c) 3.9 μs/800 ns.

By adding H^+, the ethanol solution of free ligand L turns from pale yellow to orange and at last to colorless. The change to orange results from the protonation of the bpy part, since the positive charge of H^+ will decrease the energy level of the π^* orbital of the bpy part. When the pH of the solution is small enough, the DMA part is also protonated, and the elimination of the electron donating property of the DMA part makes the ILCT transition fail to exist, so the solution turns to colorless eventually. The electronic absorption spectrum of $Ru(bpy)_2(L)^{2+}$ displays a broad and intense band centered at 470 nm (Figure 1a). Taking into account the effects resulting from binding H^+ on ligand L, this absorption band should be a superposition of ILCT and MLCT transitions since the chelation to Ru(II) of L can also red-shift its ILCT transitions. By adding acid to the solution of the complex, the absorbance in the CT region is reduced by half, and the absorption maximum is slightly blue-shifted (Figure 1b), which indicates that the ILCT transitions collapse due to the protonation of the DMA part.

For excitation at any wavelength in the CT absorption region, only one emission band centered at 617 nm can be observed at room temperature in steady-state emission spectra (Figure 1c,d). In consideration of the position, the structureless shape, and the remarkable solvent dependence ($\lambda_{max} =$ 616 nm in MeCN and $\lambda_{max} = 585$ nm in $CHCl_3$), the origin of this emission band should be the luminescence of the ^{3}MLCT state. Due to the high luminescence quantum yield, a contribution of $Ru(bpy)_3^{2+}$, a possible impurity which may form in the synthesis of $Ru(bpy)_2(L)^{2+}$, to this ^{3}MLCT emission band could not be exclusively ruled out though there is a blue-shift for the MLCT emission of pure $Ru(bpy)_3^{2+}$ (606 nm in MeCN). Although the ILCT transition can absorb some proportions at the excitation wavelength, there is no observation of ^{1}ILCT or ^{3}ILCT luminescence. The absence of ^{1}ILCT fluorescence is not surprising since the intramolecular quenching of the ^{1}ILCT excited state is fast by singlet−singlet energy transfer to the ^{1}MLCT state or by intersystem crossing to the ^{3}ILCT state, which is enhanced in the presence of Ru(II) (heavy atom effect).[14] The ^{3}ILCT luminescence cannot be well-resolved even in deaerated conditions, in which the quenching of the ^{3}ILCT state by O_2 is avoided, which suggests that the intrinsic emission quantum yield of the ^{3}ILCT state at room temperature is very low and its emission is buried in the relative strong ^{3}MLCT emission band. The low emission quantum yield of ^{3}ILCT at room temperature may be due to the effective nonradiative decay by way of the rotation of the double bond of L in the excited state. The much clearer resolution of ^{3}ILCT emission at 77 K than at room temperature by the time-resolved technique agrees with this assumption (see following description). The emission quantum yield of $Ru(bpy)_2(L)^{2+}$ in degassed CH_3CN solution is much smaller than that of $Ru(bpy)_2(dmb)^{2+}$ ($\Phi_{em} = 0.003$ and 0.084, respectively, where dmb is 4,4′-dimethyl-2,2′-bipyridine). As indicated in Figure 1a,b, about 50% absorption in the CT region comes from the MLCT transitions, so a luminescence quantum yield of 0.042 can be expected for $Ru(bpy)_2(L)^{2+}$ if the presence of ^{1}ILCT and ^{3}ILCT has no effect on the decay kinetics of the MLCT state. The much low emission quantum yield indicates that ^{3}MLCT luminescence is quenched greatly due to the involvement of the ILCT state. This is further confirmed by the fact that the protonation of the complex increases the emission intensity greatly (Figure 1e).

In order to explore the nature of the excited states, time-resolved emission spectra with laser excitation at 460 nm were recorded in 4:1 ethanol/methanol solutions degassed by high purity argon (Figure 2). The intensity-normalized early- and late-gated emission spectra indicate that two separate excited states are involved. The spectrum measured at 0.66 μs after the laser pulse shows an emission band centered at 615 nm with a shoulder at about 680 nm. At longer delay times (1.6 μs, spectrum in Figure 2b), the emission intensity of the shoulder increases, and two comparable emission bands are observed. Finally, at the delay time up to 3.9 μs, the low energy emission band becomes dominant, and the band at 615 nm appears only as a shoulder. Compared with the steady-state emission spectra, the higher energy emission band should come from the ^{3}MLCT state. The emission lifetime measured at the blue edge of this emission band ($\tau_{em} = 851$ ns) also locates in the normal region of ^{3}MLCT decay. The observed emission band at 680 nm provides direct evidence for the existence of another excited state. The much longer lifetime for this band ($\tau_{em} =$ 1115 ns) excludes the possibility of ^{1}ILCT emission. The appropriate assignment for this emission band should be the ^{3}ILCT excited state. The obtained emission lifetime for the

---

(14) Wilson, G. J.; Launikonis, A.; Sasse, W. H. F.; Mau, A. W. H. *J. Phys. Chem A* **1997**, *101*, 4860−4866.

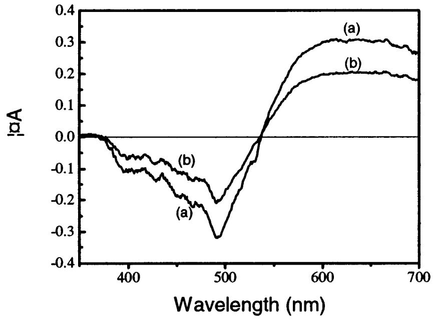


Figure 3. Transient absorption spectra of the complex in EtOH/MeOH (4:1) solution following pulsed laser excitation (532 nm) of the complex at the delay time of 200 ns (a) and 640 ns (b).

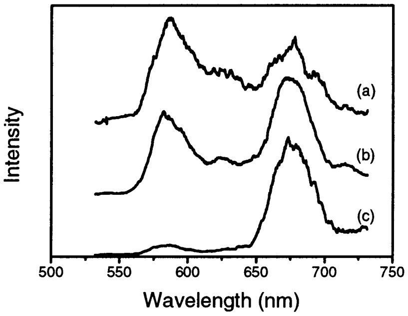


Figure 4. Time-resolved emission spectra ($\lambda_{\mathrm{exc}} = 460$ nm) in EtOH/MeOH (4:1) glass at 77 K measured with the following delay/gate width settings: (a) 4.4 μs/200 ns; (b) 8.5 μs/1 μs; (c) 19 μs/3 μs.

^{3}ILCT excited state is much shorter than those of a pyrene-included metal diimine complex,[10] but in a terpyridine complex of Pt(II), Pt(4′-NMe$_2$-trpy)Cl$^+$, an ^{3}ILCT emission with a lifetime on the order of a microsecond at room temperature has been reported.[15] The different decay kinetics of the two emission bands, which make the weak ^{3}ILCT luminescence observable, shows that the ^{3}ILCT and ^{3}MLCT excited states are nonthermally equilibrated even at room temperature. This phenomenon is different from that of other systems, in which the coexisted excited states are thermally equilibrated at room temperature.

Nanosecond transient absorption spectra of the complex following pulsed laser excitation at 532 nm are shown in Figure 3. The spectra exhibit a bleaching of the MLCT absorption in the region from 385 to 535 nm with a maximum at 475 nm. At longer wavelengths, the complex has a broad and much stronger positive absorption that differs from other Ru(II) diimine complex such as [Ru(dmb)$_3$]$^{2+}$,[5] in which only a very weak absorption band in this region was observed. The much lower energy of this absorption band excludes the possibility of the triplet−triplet absorption of *N*,*N*-dimethylaniline (DMA) in ligand L.[16] Moreover, this absorption band failed to appear when the N atom on the DMA part was protonated and the ILCT transition did not exist. So it can be assigned to the triplet−triplet absorption of the ILCT states. Some pyrene-containing Ru(II) complexes with ILCT states were also proven to possess the similar transient absorption feature.[10] The decay of the red absorption region is monoexponential with a lifetime about 1113 ns, and the agreement with the emission lifetime of the low energy band in Figure 2 suggests that they originate from the same excited state.

The time-resolved emission spectra at 77 K in 4:1 ethanol/methanol solutions are shown in Figure 4. The intensity-normalized spectra show two well-resolved emission bands. The lower energy emission band gradually dominates with prolonged delay time; at a much longer delay time of 19 μs, the 585 nm emission band appears as a much weaker band. In the overall process, there is no change in the emitting species, but the emission lifetimes have large differences. Taking into account the dependence of the ^{3}MLCT emission band on the medium rigidity and comparing it with that of another Ru(II) diimine complex,[17] we find that the band with a maximum at 585 nm could be attributed to the ^{3}MLCT luminescence. The emission decay measured at the blue edge of this emission band exhibits a lifetime of 4.7 μs and locates in the normal region of ^{3}MLCT emission decay (1−5 μs) at 77 K. The rather strong emission band at longer delay times shows a lifetime extending to 48 μs. It is more appropriate to assign the 670 nm emission bands to the ^{3}ILCT state, whose emission maximum blue shifts by about 10 nm upon decreasing the temperature from room temperature to 77 K. The large difference in the lifetimes of the two emission bands proves that these two excited states are nonthermally equilibrated at 77 K and relax independently to the ground states as is the case at room temperature.

In conclusion, simultaneous ^{3}MLCT and ^{3}ILCT emission of a Ru(II) diimine complex was observed for the first time at room temperature by the use of time-resolved luminescence spectroscopy. Although multiple luminescence results for MLCT complexes of Rh(III), Ir(III), Re(I), and Cu(I) in low-temperature rigid glasses have been reported, dual emission for Ru(II) diimine complexes is generally not observed. Different from other systems, these two excited states are nonthermally equilibrated even at room temperature. The presence of ILCT states, in addition to MLCT states, provides an additional approach for tuning excited-state energies in metal diimine complexes.

Acknowledgment. This work was financially supported by NNSFC and the Minister of Science and Technology (29971031, 20073050, G2000028204).

IC026070J

---

(15) Crites, D. K.; Stacy, E. M.; Mcmillin, D. R. *Inorg. Chim. Acta* **1998**, *273*, 346−353.

(16) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker Inc.: New York, 1973.

(17) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583−5593.