

Solid State Effect on the Phosphorescence Spectrum of a Tris(3,3'-biisoquinoline)ruthenium(II) Salt

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A broad and red-shifted emission spectrum was observed in the neat crystal of $[\text{Ru}(i\text{-biq})_3](\text{PF}_6)_2$ ($i\text{-biq} = 3,3'\text{-biisoquinoline}$) in contrast to a sharp $^3\pi\pi^*$ -type emission spectrum in a dilute glassy solution. On the basis of the analyses of the concentration dependence of the emission spectrum and the X-ray crystal structure, the characteristic emission of the crystal was attributed to $\pi\text{-}\pi$ interactions between the $i\text{-biq}$ ligands of the adjacent complexes.

Many (polypyridine)ruthenium(II) complexes have been actively synthesized and investigated on their photochemical and photophysical properties by means of various techniques.¹⁾ Among such ruthenium complexes, the tris(3,3'-biisoquinoline)ruthenium(II) ion, $[\text{Ru}(i\text{-biq})_3]^{2+}$, is an unique complex because its emissive state is a ligand-centered $^3\pi\pi^*$ state, whereas the lowest excited singlet state is a $^1\text{d}\pi^*$ metal-to-ligand charge transfer state. In the course of the spectroscopic investigation of the complex, we have found the fact that the crystal of $[\text{Ru}(i\text{-biq})_3](\text{PF}_6)_2$ gives a red emission at 77 K in contrast to a yellow-green emission in a dilute glassy solution, which is a so-called solid state effect. In this letter, we report the phosphorescence spectra, a concentration dependence of the spectrum in acetonitrile, and an X-ray structural analysis of the crystal in order to clarify the cause of the solid state effect on the emission spectra of $[\text{Ru}(i\text{-biq})_3](\text{PF}_6)_2$.

3,3'-Biisoquinoline was prepared according to the literature.²⁾ Mp 205-206 °C. $[\text{Ru}(i\text{-biq})_3](\text{PF}_6)_2$ was prepared by the similar method reported previously.³⁾ Recrystallization from acetonitrile/ethanol gave an orange crystal of $[\text{Ru}(i\text{-biq})_3](\text{PF}_6)_2 \cdot 1.5\text{CH}_3\text{CN}$. Anal. Found: C, 55.99; H, 3.51; N, 8.56%; Calcd for $\text{RuP}_2\text{F}_{12}\text{N}_6\text{C}_{54}\text{H}_{36} \cdot 1.5\text{CH}_3\text{CN}$: C, 56.05; H, 3.34; N, 8.60%. ^1H NMR (270 MHz, $(\text{CD}_3)_2\text{CO}$), δ 9.40(s), 9.17(s), 8.23 (d, $J = 8.3$ Hz), 7.91 (dd, $J = 8.3$, 6.8 Hz), 7.79 (d, $J = 8.3$ Hz), 7.68 (dd, $J = 8.3$, 8.3 Hz), 7.41 (dd, $J = 8.3$, 6.8 Hz), 7.29 (d, $J = 8.3$ Hz), 7.18 (dd, $J = 8.3$, 6.8 Hz), 7.07 (d, $J = 8.3$ Hz), 6.96 (dd, $J = 8.3$, 6.8 Hz), 6.85 (d, $J = 8.3$ Hz), 6.74 (dd, $J = 8.3$, 6.8 Hz), 6.63 (d, $J = 8.3$ Hz), 6.52 (dd, $J = 8.3$, 6.8 Hz), 6.41 (d, $J = 8.3$ Hz), 6.30 (dd, $J = 8.3$, 6.8 Hz), 6.19 (d, $J = 8.3$ Hz), 6.08 (dd, $J = 8.3$, 6.8 Hz), 5.97 (d, $J = 8.3$ Hz), 5.86 (dd, $J = 8.3$, 6.8 Hz), 5.75 (d, $J = 8.3$ Hz), 5.64 (dd, $J = 8.3$, 6.8 Hz), 5.53 (d, $J = 8.3$ Hz), 5.42 (dd, $J = 8.3$, 6.8 Hz), 5.31 (d, $J = 8.3$ Hz), 5.20 (dd, $J = 8.3$, 6.8 Hz), 5.09 (d, $J = 8.3$ Hz), 4.98 (dd, $J = 8.3$, 6.8 Hz), 4.87 (d, $J = 8.3$ Hz), 4.76 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Hz), -24.80 (dd, $J = 8.3$, 6.8 Hz), -24.89 (d, $J = 8.3$ Hz), -24.96 (dd, $J = 8.3$, 6.8 Hz), -25.05 (d, $J = 8.3$ Hz), -25.12 (dd, $J = 8.3$, 6.8 Hz), -25.21 (d, $J = 8.3$ Hz), -25.28 (dd, $J = 8.3$, 6.8 Hz), -25.37 (d, $J = 8.3$ Hz), -25.44 (dd, $J = 8.3$, 6.8 Hz), -25.53 (d, $J = 8.3$ Hz), -25.60 (dd, $J = 8.3$, 6.8 Hz), -25.69 (d, $J = 8.3$ Hz), -25.76 (dd, $J = 8.3$, 6.8 Hz), -25.85 (d, $J = 8.3$ Hz), -25.92 (dd, $J = 8.3$, 6.8 Hz), -26.01 (d, $J = 8.3$ Hz), -26.08 (dd, $J = 8.3$, 6.8 Hz), -26.17 (d, $J = 8.3$ Hz), -26.24 (dd, $J = 8.3$, 6.8 Hz), -26.33 (d, $J = 8.3$ Hz), -26.40 (dd, $J = 8.3$, 6.8 Hz), -26.49 (d, $J = 8.3$ Hz), -26.56 (dd, $J = 8.3$, 6.8 Hz), -26.65 (d, $J = 8.3$ Hz), -26.72 (dd, $J = 8.3$, 6.8 Hz), -26.81 (d, $J = 8.3$ Hz), -26.88 (dd, $J = 8.3$, 6.8 Hz), -26.97 (d, $J = 8.3$ Hz), -27.04 (dd, $J = 8.3$, 6.8 Hz), -27.13 (d, $J = 8.3$ Hz), -27.20 (dd, $J = 8.3$, 6.8 Hz), -27.29 (d, $J = 8.3$ Hz), -27.36 (dd, $J = 8.3$, 6.8 Hz), -27.45 (d, $J = 8.3$ Hz), -27.52 (dd, $J = 8.3$, 6.8 Hz), -27.61 (d, $J = 8.3$ Hz), -27.68 (dd, $J = 8.3$, 6.8 Hz), -27.77 (d, $J = 8.3$ Hz), -27.84 (dd, $J = 8.3$, 6.8 Hz), -27.93 (d, $J = 8.3$ Hz), -28.00 (dd, $J = 8.3$, 6.8 Hz), -28.09 (d, $J = 8.3$ Hz), -28.16 (dd, $J = 8.3$, 6.8 Hz), -28.25 (d, $J = 8.3$ Hz), -28.32 (dd, $J = 8.3$

6.8 Hz); ^{13}C NMR (68 MHz, $(\text{CD}_3)_2\text{CO}$), δ 156.3, 151.2, 136.4, 133.7, 130.8, 130.4, 128.6, 128.2, 121.9.

The NMR data indicate that six isoquinoline units of the complex are equivalent in the solution. Emission spectra were obtained with a Hitachi 850 spectrofluorimeter. For the solid state spectrum, neat crystals mounted on a quartz cell with silicon grease was used.

Figure 1 shows emission spectra of $[\text{Ru}(i\text{-biq})_3](\text{PF}_6)_2 \cdot 1.5\text{CH}_3\text{CN}$ in glassy ethanol/methanol (4:1 v/v) and in the neat crystals at 77 K. The relatively sharp structured emission of the glassy solution (a) is characteristic of the $^3\pi\pi^*$ -type emission that is already reported.⁴⁾ In contrast, the emission spectrum of the crystals (b) is very broad and red-shifted. Such a remarkable difference would be caused by either an intramolecular factor such as distortion of the ligand or the coordination structure, or an intermolecular factor such as interligand interaction. Figure 2 shows emission spectra of the complex observed in acetonitrile at 77 K under various concentrations. With increasing concentration, the emission spectrum varied remarkably from the sharp structured spectrum to the broad and red-shifted one decreasing in intensity to a few % of its initial one. The spectra at the higher concentrations (d and e) are very similar to that of the crystal. The excitation spectrum measured at 540 nm of the spectrum c in Fig. 2 was consistent with the absorption spectrum in the dilute solution, while a broad and unstructured excitation spectrum was observed at 640 nm, indicating that the sharp and broad emissions originate from different species depending on the concentration. The corresponding concentration dependence of the emission spectrum was also observed in a liquid acetonitrile solution at room temperature, though the spectra were much broader. This fact excludes the possibility that the red-shifted emission in acetonitrile at 77 K is due to a precipitation of the crystals. Thus, it is likely that the intermolecular interactions make the emission spectra broad and red-shifted both in the concentrated solution

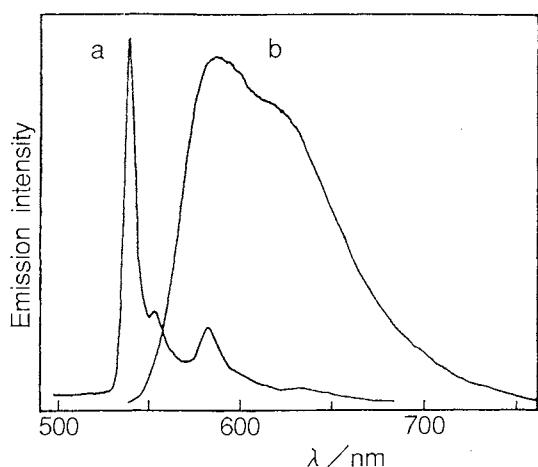


Fig. 1. Emission spectra of $[\text{Ru}(i\text{-biq})_3](\text{PF}_6)_2 \cdot 1.5\text{CH}_3\text{CN}$ at 77 K: (a) 5×10^{-6} mol dm^{-3} in ethanol/methanol (4:1 v/v), (b) neat crystals. $\lambda_{\text{ex}} = 330$ nm.

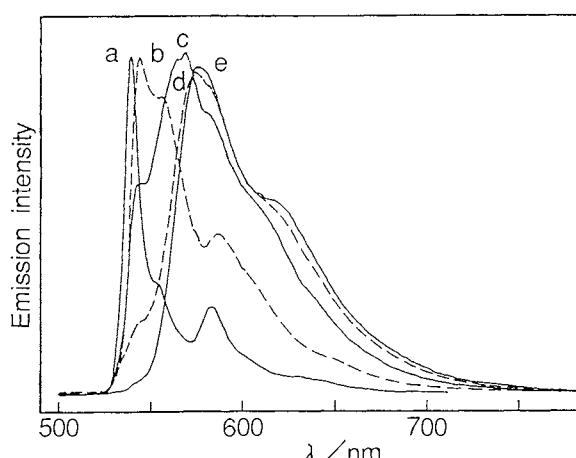


Fig. 2. Emission spectra on various concentrations of $[\text{Ru}(i\text{-biq})_3]^{2+}$ in acetonitrile at 77 K: (a) 1.9×10^{-6} , (b) 1.2×10^{-5} , (c) 3.0×10^{-5} , (d) 1.5×10^{-4} , (e) 1.7×10^{-3} mol dm^{-3} . $\lambda_{\text{ex}} = 330$ nm.

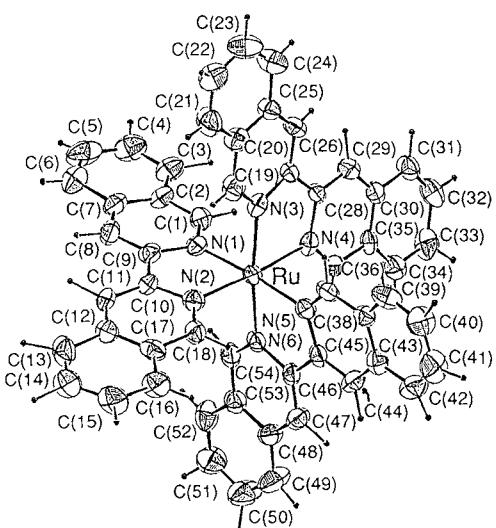


Fig. 3. ORTEP drawing of the $[\text{Ru}(i\text{-biq})_3]^{2+}$ ion with 50% probability ellipsoids for non-hydrogen atoms.

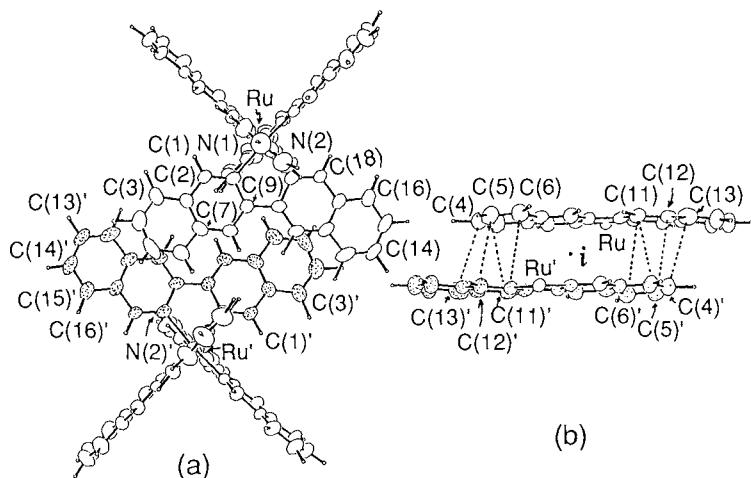


Fig. 4. (a) Arrangement of two adjacent $[\text{Ru}(i\text{-biq})_3]^{2+}$ ions related by an inversion center. (b) Two $(i\text{-biq})\text{Ru}$ parts viewed from the direction along the $i\text{-biq}$ plane. The interligand distances are as follows: $\text{C}(4)\cdots\text{C}(13') = 3.35(4)$, $\text{C}(5)\cdots\text{C}(13') = 3.56(4)$, $\text{C}(5)\cdots\text{C}(12') = 3.47(4)$, and $\text{C}(6)\cdots\text{C}(11') = 3.58(3)$ Å.

and crystal. The result of the X-ray analysis⁵⁾ has confirmed an existence of the intermolecular interactions in the neat crystal. Figure 3 shows a perspective view of $[\text{Ru}(i\text{-biq})_3]^{2+}$. As is obvious from the space group ($P2_1/n$), three $i\text{-biq}$ ligands are crystallographically independent of one another. The coordination bond lengths and angles, however, are within normal ranges⁶⁾ and similar to those of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ (bpy = 2,2'-bipyridine) in which the three ligands are exactly equivalent.⁷⁾ No abnormal values are obtained also for the bond lengths and angles of the $i\text{-biq}$ ligands though they are slightly deformed from the planarity. Such a small deformation of the $i\text{-biq}$ ligands has been often observed in the complexes with bpy-type ligands.⁸⁾ On the other hand, an environment of the three $i\text{-biq}$ ligands of the $[\text{Ru}(i\text{-biq})_3]^{2+}$ ion is considerably different from the other cases. In this case, one $i\text{-biq}$ ligand in the complex is close to the $i\text{-biq}$ ligand of the adjacent complex being their molecular planes parallel each other (Fig. 4). They are related by the inversion center as shown in Fig. 4b. There are a lot of short distances among the atoms as indicated by broken lines. They are short enough to allow overlaps of π orbitals between adjacent complexes because the sum of the van der Waals radii of the aromatic carbon atoms is estimated to be around 3.5 Å. As shown in Fig. 4, the parallel orientation of the two adjacent $i\text{-biq}$ ligands provides an overlap of HOMO and HOMO just in phase, whereas HOMO and LUMO overlaps out of phase.⁹⁾ The interactions of two HOMO's make an energy difference between π and π^* orbitals smaller than that of the isolated complex, resulting in a red shifted emission. The other two $i\text{-biq}$ ligands in $[\text{Ru}(i\text{-biq})_3]^{2+}$ keep van der Waals contacts with adjacent ligands in the crystal. Therefore, the spectral features of the crystal can be explained in terms of the $\pi\text{-}\pi$ interactions between the

ligands of the adjacent complexes. Similar π - π interactions affecting the emission properties have been reported for the (polypyridine)platinum complex, $[\text{Pt}(\text{phen})_2]^{2+}$ (phen = 1,10-phenanthroline).¹⁰⁾ It is well known that square-planar platinum(II) complexes are easy to stack showing "solid state effects". For (poly pyridine)ruthenium(II) complexes with the octahedral configuration, however, this is the first example that the solid state effect is attributed to the π - π interactions between adjacent complex ions. Further experiments on emission decay behavior and temperature dependence of the emission spectrum are now in progress.

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- 6) Bond lengths (Å) and angles (degree) around the ruthenium atom: Ru - N(1) = 2.07(2), Ru - N(2) = 2.06(2), Ru - N(3) = 2.11(2), Ru - N(4) = 2.08(2), Ru - N(5) = 2.07(2), Ru - N(6) = 2.06(2), N(1) - Ru - N(2) = 80.0(7), N(3) - Ru - N(4) = 79.0(6), N(5) - Ru - N(6) = 80.2(6).
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