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Tuning of Luminescence Spectra of Neutral Ruthenium(II) Complexes by Crystal Waters

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Neutral ruthenium(II) complexes [RuLL′(CN)$_2$] (L, L′ = bpy, dmb, dbb; bpy = 2,2′-bipyridine, dmb = 4,4′-dimethyl-2,2′-bipyridine, dbb = 4,4′-*tert*-butyl-2,2′-bipyridine) were prepared, and the luminescence characteristics of the complexes in the solid state were measured. The luminescence was tuned by crystal waters included in the crystals; for example, [Ru(dbb)$_2$(CN)$_2$]•2H$_2$O, [Ru(dbb)$_2$(CN)$_2$]•H$_2$O, and [Ru(dbb)$_2$(CN)$_2$] emit luminescence at 640, 685, and 740 nm, respectively.

Recently, photo- and material chemists have been fascinated with the luminescence vapochromic behavior of Pt(II) complexes because of their potential application in volatile organic compound (VOC) sensing. Luminescence changes upon exposure of Pt(II) complex crystals to VOCs have been reported in several scientific papers.[1−4] The molecular structures of these Pt(II) complexes are mostly planar; Pt(II)−Pt(II) and $\pi-\pi$ interactions between ligands were observed in the crystals.[5] The crystals contains infinite stacks of Pt(II) molecules; VOCs were sorbed into the channels along a Pt−Pt chain.[1a] This sorption into the crystal lattice strengthened the Pt−Pt interaction and caused a dramatic growth in luminescence assigned to an MMLCT transtion.[3] The linear-chain polymer $\{Tl[Au(C_6Cl_5)_2]\}_n$ also showed a remarkable color-emission response to VOC vapor.[6a] The polymer−VOC complex was formulated as $\{Tl(L)_2[Au(C_6Cl_5)_2]\}_n$ in which the volatile compounds (L) coordinated to the Tl(I) center.[6b] Ford et al. reported solvent- and solvent-vapor-induced luminescence changes of the copper(I) complex due to the polymer−tetramer isomerization.[7] In this communication, we present the luminescence vapochromism of solid [Ru(bpy)$_2$(CN)$_2$] (bpy = 2,2′-bipyridine).

Solid-state luminescence spectra of [RuLL′(CN)$_2$] (L, L′ = bpy, dmb, dbb; dmb = 4,4′-dimethyl-2,2′-bipyridine, dbb = 4,4′-*tert*-butyl-2,2′-bipyridine) were measured at room temperature. The samples were prepared as thin films on glass substrates by cast coating or spin coating, and the glasses were put into cuvettes for luminescence measurements. Luminescence spectra are dependent on ligand; the bulkier the ligand is, the more the luminescence shifts to the low-energy region, and there is a tendency that the luminescence of [RuLL′(CN)$_2$] is observed in the low-energy region compared to that of [RuL$_2$(CN)$_2$]. The luminescence spectra were recorded under the saturation water-vapor pressure (P_{H_2O} =3000 Pa at 298 K), because the reproducibility of each spectrum was poor unless the moisture content in the cuvette was controlled. The luminescence of the [Ru(dbb)$_2$(CN)$_2$] thin film was the most sensitive to moisture. As shown in Figure 1, the luminescence of [Ru(dbb)$_2$(CN)$_2$] peaked at 640 nm at P_{H_2O} = 3000 Pa, and the peak red-shifted as the water-vapor pressure in the cuvette decreased. The luminescence spectrum of [Ru(dbb)$_2$(CN)$_2$] was easily tuned under a variety of water-vapor pressures. The spectral change was a reversible process, that is, the luminescence spectrum shifted to the high-energy region and grew larger in intensity with increasing vapor pressure, and vice versa. The same results were observed for other complex crystals. Recrystallization of [Ru(dbb)$_2$(CN)$_2$] from water gave bright orange fine needles; the crystals emitted luminescence peaking at around 640 nm. When the Ru(II) complex was recrystallized from chloroform, dark red crystals were obtained. Luminescence of the crystals was observed at 685 nm. Elemental analyses revealed the compositions of the bright orange and dark red crystals to be [Ru(dbb)$_2$(CN)$_2$]•

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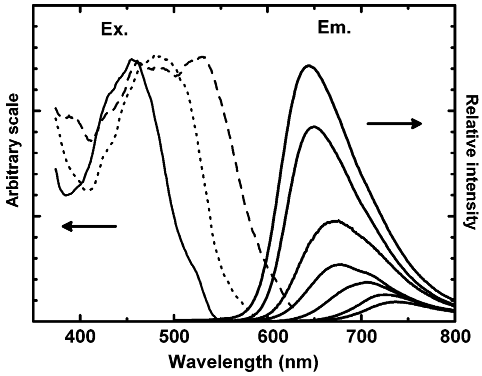

Figure 1. Luminescence emission and excitation spectra of $[Ru(dbb)_2(CN)_2]$ thin film. The emission spectra were measured under a variety of water-vapor pressures ($P_{H_2O} = 3000, 300, 30, 3, 0.3, 0.03, 0.003$ Pa). The excitation spectra were recorded with monitoring at the respective emission peaks for $[Ru(dbb)_2(CN)_2]\cdot 2H_2O$ (—), $[Ru(dbb)_2(CN)_2]\cdot H_2O$ (···), and $[Ru(dbb)_2(CN)_2]$ (− − −).

$2H_2O$ and $[Ru(dbb)_2(CN)_2]\cdot H_2O$, respectively.[8] This clearly shows that the crystal water affects the color and luminescence of the complex crystals. A luminescence spectrum of the crystal evacuated under a vacuum red-shifted to 740 nm. Elemental analysis showed that this crystal had no water of hydration.[9] This result was supported by an ^1H NMR spectrum in which no water signal was detected; the samples for ^1H NMR measurements were prepared as acetone-d_6 solutions in a vacuum line. It was concluded that $[Ru(dbb)_2(CN)_2]\cdot 2H_2O$, $[Ru(dbb)_2(CN)_2]\cdot H_2O$, and $[Ru(dbb)_2(CN)_2]$ emit luminescence at 640, 685, and 740 nm, respectively. Excitation spectra of the complex crystals are also shown in Figure 1. The monitoring wavelengths were set at the respective emission peaks for taking the spectra. MLCT bands in the spectra are blue-shifted with increasing number of waters of hydration. Excitation spectra profiles are independent of monitoring wavelength. The complex crystals, which emitted luminescence at $\lambda_{max} = 640-740$ nm in Figure 1, seemed to be composed of $[Ru(dbb)_2(CN)_2]\cdot 2H_2O$, $[Ru(dbb)_2(CN)_2]\cdot H_2O$, and $[Ru(dbb)_2(CN)_2]$. However the luminescence emission spectra could not be reconstructed with the superposition of these three components, and luminescence decays after laser excitation were not in agreement with sums of exponential curves. The results suggest that the excitation-energy relaxation process of the crystals is governed by a complicated mechanism including energy migration over the components, energy transfer from dihydrate to monohydrate and from monohydrate to anhydrate, etc.

^1H NMR spectroscopy was a useful tool for counting waters of hydration in $[Ru(dbb)_2(CN)_2]\cdot nH_2O$. When the crystal is dissolved in a dry solvent, the intensity of water in ^1H NMR spectrum should be proportional to the number of waters of hydration. The proton intensity of water was evaluated relative to that of the *tert*-butyl groups of the ligands as an internal standard: δ 1.33 (18H), 1.51 (18H).

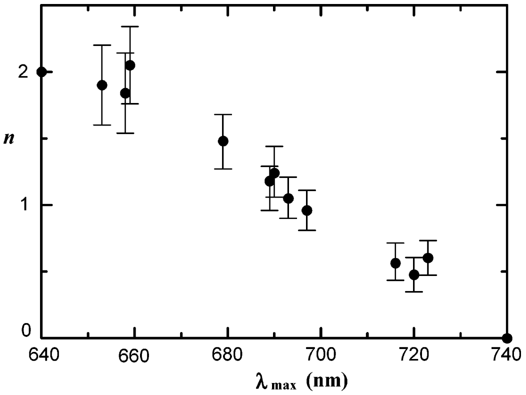

Figure 2. Plot of the number of crystal waters (n) vs the emission peak wavelength (nm) for the $[Ru(dbb)_2(CN)_2]$ thin film under a variety of water-vapor pressures.

Figure 2 shows a plot of the number of crystal waters (n) vs the luminescence peak for $[Ru(dbb)_2(CN)_2]\cdot nH_2O$. The result clearly indicates that the molar ratio of water molecules to the Ru(II) complex is in the range of $0-2$ and is in good agreement with the results of elemental analysis mentioned above. It is concluded that the $[Ru(dbb)_2(CN)_2]$ crystal absorb water molecules from the air under high water-vapor pressure and release the water into the air under low water-vapor pressure. The water sorption into the complex crystal was expressed by the Langmuir isotherm $\theta = Kp/(1 + Kp)$, where θ ($= n/n_{max}$) denotes the fraction of sorbing sites occupied and K and p are the equilibrium constant and water-vapor pressure, respectively.[10] Rearranging the equation as $p/n = p/n_{max} + 1/(Kn_{max})$, p/n was plotted as a function of p, and a straight line was obtained. From the slope and the intercept, K and n_{max} were evaluated as $K = 0.2$ Pa^{-1} and $n_{max} = 2.2$, respectively. It is clearly indicated that the maximum number of crystal waters (n_{max}) is 2, and the capability of the complex for water sorption is relatively high.

The protonation reaction of excited $[Ru(bpy)_2(CN)_2]$ in solution was previously reported by Demas[11] and Scandola.[12] According to their studies, protonation of the CN ligand(s) caused a significant blue shift of the luminescence spectrum as a result of the sequential protonation of the CN ligands. The luminescence peaked at around 670 nm for $[Ru(bpy)_2(CN)_2]$ and 580 nm for $[Ru(bpy)(CN)(CNH)]^+$. By analogy of the results, a specific interaction between the CN ligand(s) and water molecule(s) such as hydrogen bonding is expected for the $[Ru(dbb)_2(CN)_2]\cdot nH_2O$ ($n > 0$) system. The CN stretching bands (ν_{CN}) observed at 2067.4 and 2052.9 cm^{-1} for $[Ru(bpy)_2(CN)_2]$[13] were found to be sensitive to the protonation and metalation. Proton and metal attachment to the CN groups caused a high-frequency shift of ν_{CN}. It was found that $\nu_{CN} = 2103.0$ and 2072.8 cm^{-1} for $[Ru(bpy)_2(CNH)_2]^{2+}$.[14] Bignozzi and Scandola reported ν_{CN}

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(8) Anal. Calcd for $[Ru(dbb)_2(CN)_2]\cdot H_2O$ C 64.47, H 7.12, N 11.75; found C 64.36, H 6.93, N 11.91. Calcd for $[Ru(dbb)_2(CN)_2]\cdot 2H_2O$ C 62.87, H 7.22, N 11.56; found C 62.87, H 7.26, N 11.75.

(9) Anal. Calcd for $[Ru(dbb)_2(CN)_2]$ C 66.15, H 7.01, N 12.18; found C 66.13, H 7.05, N 12.18.

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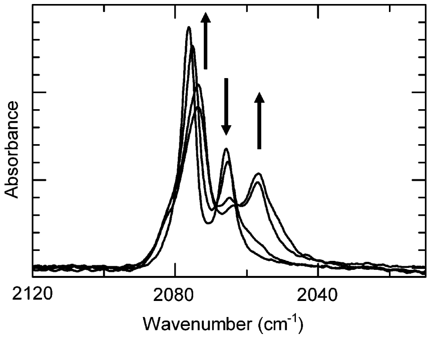

Figure 3. FTIR spectra of $[Ru(dbb)_2(CN)_2]$ thin films under a variety of water-vapor pressures. The number of crystal waters was adjusted as each luminescence was observed at 650, 660, 684, and 700 nm, respectively. The bands were grown and bleached with increasing crystal water as indicated by solid arrows.

Table 1. CN Stretching Frequencies (ν_{CN}) for $[RuL_2(CN)_2]$

compd	ν_{CN} (cm^{-1})
$[Ru(dbb)_2(CN)_2]\cdot H_2O^a$	2065, 2076
$[Ru(dbb)_2(CN)_2]\cdot 2H_2O^a$	2056, 2073
$[Ru(dbb)_2(CN)_2]^b$	2066, 2077
$[Ru(bpy)_2(CN)_2]^{b,c}$	2052.9, 2067.4
$[Ru(bpy)_2(CNH)_2]^{2+\,d}$	2072.8, 2103.0
$[Ru(bpy)_2(CN)(CN{-}Pt(dien)_2)]^{2+\,e}$	2058, 2108
$[Ru(bpy)_2(CN{-}Pt(dien)_2)_2]^{4+\,e}$	2108, 2129
$[Ru(bpy)_2(CN)(CN{-}OsO_2(mes))]^{2+\,f}$	2058, 2108

[a] Values obtained by the spectral fitting. [b] In CH_3CN. [c] Reference 13. [d] Reference 14. [e] Reference 15. [f] Reference 16.

$= 2108$ and 2058 cm^{-1} for $[Ru(bpy)_2(CN)(CN{-}Pt(dien)_2)]^{2+}$ and $\nu_{CN} = 2129$ and 2108 cm^{-1} for $[Ru(bpy)_2(CN{-}Pt(dien)_2)_2]^{4+}$,[15] and Cheng et al. reported $\nu_{CN} = 2088.5$ and 2072.8 cm^{-1} for $[Ru(bpy)_2(CN)(CN{-}OsO_2(mes))]$.[16] FTIR spectra of $[Ru(dbb)_2(CN)_2]$ in the solid state are shown in Figure 3. The solid samples of $[Ru(dbb)_2(CN)_2]$ for FTIR measurements were prepared on a CaF_2 window under various water-vapor pressures and adjusted to emit luminescence at 650, 660, 684, and 700 nm, that is, to include 2, 2−1, 1, and 1−0 crystal waters, respectively. When two crystal waters were included, CN stretching bands were observed at $\nu_{CN} = 2073$ and 2056 cm^{-1}. With decreasing number of crystal waters, the band at 2056 cm^{-1} decreased in intensity, the band at 2073 cm^{-1} shifted to a high-frequency region, and a new band appeared at 2065 cm^{-1}. The FTIR results are in good agreement with the luminescence results: the spectral change is attributed to the water sorption into the crystal. Deconvolution of the spectra into individual components gave spectra of $[Ru(dbb)_2(CN)_2]\cdot 2H_2O$ and $[Ru(dbb)_2(CN)_2]\cdot H_2O$. The CN stretching frequencies of the components are listed in Table 1 accompanied by relevant data. The anhydrate form is expected to have the highest-frequency bands among the three hydrated species. Unfortunately, an FTIR spectrum of $[Ru(dbb)_2(CN)_2]$ could not be obtained in the present work. Further evacuation was needed to obtain the spectrum of the anhydrate form; however, it was difficult to remove water molecules completely from the complex solid in the FTIR cell. In acetonitrile, where there is no hydrogen bonding between the Ru(II) complex and the solvent molecule, CN stretching bands are observed at $\nu_{CN} = 2066$ and 2077 cm^{-1}. In the case of the present work, the increase in the number of crystal waters causes a low-frequency shift of the CN stretching bands and a high-energy shift of Ru-to-dbb CT band of $[Ru(dbb)_2(CN)_2]$, unlike the metalation and protonation of $[Ru(bpy)_2(CN)_2]$. It seems that there are no strong interactions such as a bond formation between the crystal waters and the CN groups. Timpson et al.[17] reported solvent effects on UV and IR spectra of $[Ru(bpy)_2(CN)_2]$ in solution. They correlated the solvent effects with the solvent acceptor number: an increase of the solvent acceptor number caused a blue shift of the luminescence and a low-frequency shift of the CN stretching bands. It was concluded that electron-pair donation from the CN groups to the solvent in the ground state made the CN groups better π-acceptors, and $d\pi(Ru){-}\pi^*(CN)$ back-donation caused stabilization of $d\pi$ orbital energy of Ru(II) and the low-frequency shift of ν_{CN}. Because the spectral shifts are consistent with the present results, the interaction between $[Ru(dbb)_2(CN)_2]$ and the crystal waters is suggested to be similar to that between $[Ru(bpy)_2(CN)_2]$ and solvents.

We presented the tuning of color emission of Ru(II) complex solids attributed to the luminescence water−vapochromic behavior. This is the first example of vapochromism in a Ru(II) complex. The complex is a candidate as a moisture sensor. The sensitivity is very high because the luminescence spectrum of the Ru(II) complex crystal has a capability of water sensing even under 10^{-2} Pa of water-vapor pressure. However, the luminescence spectral shift due to water sorption is relatively small. Thus, a dramatic change of color emission is desired for a chemical sensing application. Elucidation of the interaction between water and the Ru(II) complex would be required for upgrade of the sensing ability. The specific interaction could be clarified by an X-ray crystallography. Because the Ru(II) complexes display color and luminescence changes in a variety of organic solvents,[18] the complex crystals are considered to have a VOC sensing capability. Study of VOC sensing using the Ru(II) complexes is underway.

Supporting Information Available: Syntheses and luminescence spectra of $[RuL_2(CN)_2]$ and $[RuLL'(CN)_2]$. Plot of p/n vs p for $[Ru(dbb)_2(CN)_2]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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