Electroluminescence Quenching Caused by a Spin-crossover Transition

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A film of a spin-crossover complex $[Fe(dpp)_2](BF_4)_2$ (dpp = 2,6-di(pyrazol-1-yl)pyridine) was embedded into the light-emitting layer of an organic electroluminescent (EL) device with chlorophyll *a*. While the EL spectrum was observed at 300 K, the spectrum could not be observed at 200 K. The temperature dependence of the EL spectra shows the quenching of the emission below 260 K, which is the spin-transition temperature of $[Fe(dpp)_2](BF_4)_2$. This suggests that the EL quenching accompanied the spin transition.

Spin-crossover complexes have attracted much interest because of their possible application to memory and display devices,[1,2] and since the discovery of LIEEST (light-induced excited spin state trapping),[3] they have also been considered candidate for photonic devices. On the other hand, drawing attention to their drastic color, magnetic, and/or electrical change, we have tried to utilize spin-crossover complexes as components for controlling the properties of organic thin film devices. Recently, we have succeeded in fabricating a thin film of a spin-crossover complex $[Fe(dpp)_2](BF_4)_2$, which shows a spin transition around 260 K, by using a simple spin-coating method with acetonitrile solution.[4] In the obtained film, changes in the absorption spectra and electrical resistance accompanying the spin transition were observed. This result suggests the possible application of a $[Fe(dpp)_2](BF_4)_2$ film to control electronic properties in organic thin film devices. Because $[Fe(dpp)_2](BF_4)_2$ is soluble to polar solvents, it is easy to embed $[Fe(dpp)_2](BF_4)_2$ into the active layer of the organic thin film devices fabricated by the wet process. In this letter, we embedded a spin-crossover complex $[Fe(dpp)_2](BF_4)_2$ into the light-emitting layer of an EL device of chlorophyll *a*. Chlorophyll *a* is a very important and well-known compound for photosynthesis, and its absorption and PL spectra in solution state have been extensively studied.[5] We have succeeded in fabricating an EL device with chlorophyll *a* using a spin-coating method.[6]

The spin-crossover complex $[Fe(dpp)_2](BF_4)_2$ was synthesized by procedures described in the literature.[7] Chlorophyll *a* was purchased from Juntec Co. and used without further purifications. The ITO substrate was soaked in acetone and washed with ultrasonic agitation for 15 min, and then a film was fabricated on the ITO substrate by spin coating with an acetonitrile solution containing $[Fe(dpp)_2](BF_4)_2$ (2.4 wt %) and chlorophyll *a* (0.8 wt %). The thickness of the obtained film was approximately 50 nm, and the AFM measurement revealed that the roughness of the surface was low (less than 5 nm). Figure 1 shows the device architecture and molecular structures. An Al cathode (300 Å) was prepared by vacuum deposition onto the film fabricated on the ITO anode. The effective area of the junction was $1.0 \times 4.0\,mm^2$. We also fabricated a reference device with a configuration of ITO/chlorophyll *a*/Al without $[Fe(dpp)_2](BF_4)_2$. We have previously reported that EL emission of chlorophyll *a* could be obtained without a hole-transport layer or electron-transport layer.[6]

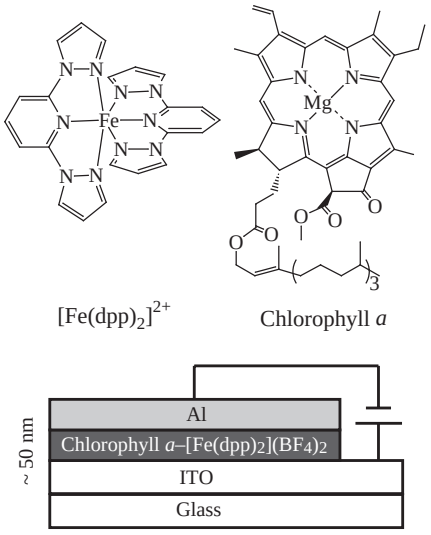

Figure 1. Molecular structures of $[Fe(dpp)_2]^{2+}$ and chlorophyll *a* and fabricated device architecture in this study.

The EL emission from the fabricated ITO/chlorophyll *a*–$[Fe(dpp)_2](BF_4)_2$/Al device under the applied voltage of 3 V was clearly observed at 300 K, and the spectrum was the same as that of the single-layer device with chlorophyll *a*.[6] However, as the temperature decreased to 200 K, the EL spectrum of chlorophyll *a* could not be observed; heating to 300 K enabled the spectrum to be obtained again. This on–off switching of the EL emission is reproducible for the heating and cooling processes. Figure 2 shows the EL spectra at different temperatures under the applied voltage of 3.5 V, and the inset depicts the temperature dependence of the EL intensity at 689 nm where the emission maximum was observed. As the temperature decreases, the intensity of the EL emission decreases, and around 260 K, the intensity becomes comparable with that of the background level. In the low-temperature region (<260 K), we tried to observe the spectrum by increasing the applied voltage. However, at 200 K, we could not detect the EL emission even when the applied voltage was increased to 5 V, where the current in the device became higher than that with 3 V at 300 K. On the other hand, for the reference device, we could observe the same EL spectrum of chlorophyll *a* at 200 K under the applied voltage of 5 V. These results suggest that the quenching of the EL emission from chlorophyll *a* below 260 K cannot be attributed to the decrease of the current and that the embedded $[Fe(dpp)_2](BF_4)_2$ in the emitting layer is responsible for the EL quenching.

Since the temperature of 260 K is almost the same to the

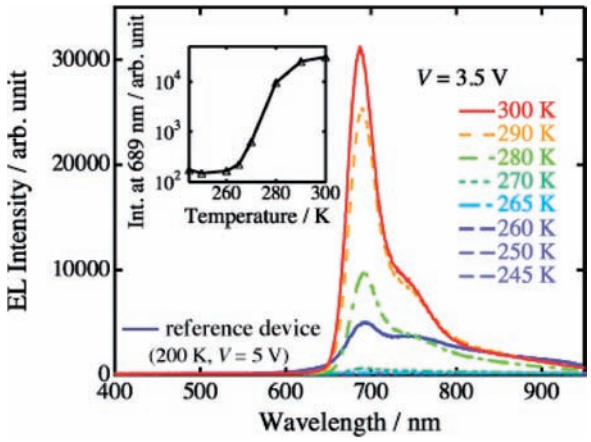

Figure 2. Electroluminescence spectra of the ITO/chlorophyll *a*–$[Fe(dpp)_2](BF_4)_2$/Al device at different temperatures under the applied voltage of 3.5 V. The spectrum of the reference device at 200 K under the applied voltage of 5 V is also depicted. The inset shows the temperature dependence of the EL intensity at 689 nm for the ITO/chlorophyll *a*–$[Fe(dpp)_2](BF_4)_2$/Al device.

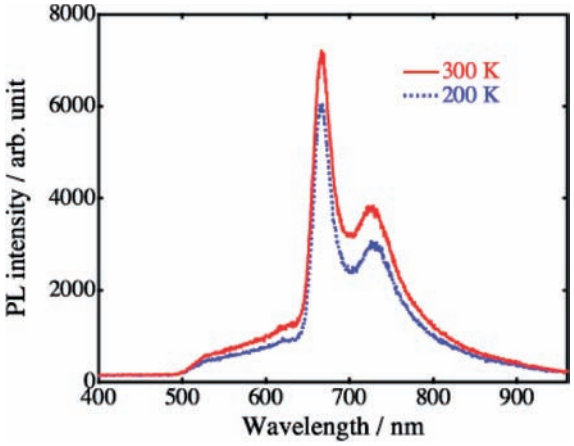

Figure 3. Photoluminescence spectra of the chlorophyll *a*–$[Fe(dpp)_2](BF_4)_2$ film at 300 K (solid line) and 200 K (dashed line).

spin-transition temperature of $[Fe(dpp)_2](BF_4)_2$ complex, it is considered that the EL quenching at 260 K is relevant to the spin transition. One possible origin is an energy transfer from excited chlorophyll *a* to $[Fe(dpp)_2](BF_4)_2$. As a result of the spin transition, the energy level of $[Fe(dpp)_2](BF_4)_2$ should change. If the energy level shifts from above to below that of the excited chlorophyll *a*, the energy transfer that leads to the nonradiative decay process can occur. In order to examine this possibility, we measured the photoluminescence (PL) spectra for the chlorophyll *a*–$[Fe(dpp)_2](BF_4)_2$ film at 300 and 200 K (see Figure 3). The film was fabricated by the same procedure as in the EL device, and the excitation wavelength was 435 nm which corresponds to the Soret band of the chlorophyll *a*. A long-pass filter (515 nm) was used and the broad emission below around 600 nm is attributable to the emission of the glass substrate. Although the PL intensity observed at 200 K was weaker than that at 300 K, the PL spectrum of chlorophyll *a* could be obtained at 200 K in contrast to the EL spectra vanishing. This result rules out the possibility that the quenching of the EL emission from chlorophyll *a* is caused by the energy transfer, and suggests the disappearance of the excited chlorophyll *a* in the EL device. We speculate that carrier injection efficiency to chlorophyll *a* is drastically changed as the spin transition of $[Fe(dpp)_2](BF_4)_2$ occurs. In other words, in the low-temperature region where $[Fe(dpp)_2](BF_4)_2$ is at a low-spin state, injected carriers pass through the insulating layer via $[Fe(dpp)_2](BF_4)_2$ without generating the excited state of chlorophyll *a*.

In summary, by embedding the spin-crossover complex $[Fe(dpp)_2](BF_4)_2$ into the light-emitting layer of an EL device with chlorophyll *a*, we achieved a drastic change of the EL intensity accompanying the spin transition of $[Fe(dpp)_2](BF_4)_2$. The EL spectrum of chlorophyll *a* observed at 300 K could not be obtained at 200 K. The on–off switching of the EL emission was reproducibly responsive to temperature changes. The PL measurement revealed that the quenching of the EL emission below 260 K, where the spin transition occurs, is due to the lack of excitation of chlorophyll *a* in the emitting layer. Since the EL emission could not be obtained even though the applied voltage was increased, the injected carriers must pass through the layer via $[Fe(dpp)_2](BF_4)_2$ at the low-temperature region. This is the first observation of a switching phenomenon in an organic thin film device accompanying the spin transition of a spin-crossover complex. The result strongly suggests that the spin-crossover complex is a versatile component for controlling device characteristics.

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