

Characteristics of organic light-emitting devices consisting of dye-doped spin crossover complex films

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ABSTRACT

Two organic light-emitting device (OLEDs) were fabricated to investigate the mechanism of electroluminescence (EL) switching accompanying the spin transition of $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ ($\text{dpp} = 2,6\text{-di}(\text{pyrazol-1-yl})\text{pyridine}$) observed in an OLED with the structure indium tin oxide (ITO)/ $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$:chlorophyll *a*/Al, consisting of a chlorophyll *a* (Chl *a*)-doped $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ film. One OLED consisted of poly(*N*-vinylcarbazole) (PVK) between an ITO electrode and the active layer, and the other contained the electron transporting dye Nile Red (NR) as an emitting dopant material instead of the hole transporting Chl *a*. In both devices ITO/PVK/ $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$:Chl *a*/Al and ITO/ $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$:NR/Al, EL emission from the dye compound was observed, irrespective of the spin state of $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$. It was determined that the EL switching accompanying the spin transition was dominated by a change in the molecular orbital level concerning electron transport in $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$.

1. Introduction

Since the discovery of spin transition between high- and low-spin states, known as the spin crossover phenomenon, spin crossover complexes have attracted much interest owing to their bistability and potential use in device applications [1]. We attempted to use spin crossover complexes to control the properties of organic thin film devices and reported a fabrication of a spin crossover complex film composed of $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ (dpp = 2,6-di(pyrazol-1-yl)pyridine) and an organic light-emitting device (OLED) composed of indium tin oxide (ITO)/ $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$:chlorophyll *a*/Al, whose active layer consists of $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ and chlorophyll *a* (Chl *a*) as a host and a dopant emitting material, respectively [2, 3]. In the ITO/ $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$:Chl *a*/Al device, reproducible on/off switching of electroluminescence (EL) emission from Chl *a* accompanying the spin transition of $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ was found. When $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ was in the high-spin state, we clearly observed light emission from Chl *a*. However, the emission was quenched below 260 K, which is the spin transition temperature of $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$. A photoluminescence study of the same mixed film of $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$

and Chl *a* revealed that the quenching was not caused by energy transfer from the excited Chl *a* to $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$, implying the absence of excited Chl *a* in the OLED device in the low-temperature region [3]. Recently, in an EL spectra study of an ITO/ $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$:Chl *a*/Al device at low temperatures, we observed a broad, weak band at around 530 nm attributable to emission from the ITO electrode [4]. Because the highest occupied molecular orbital (HOMO) energy level of Chl *a* is almost the same as the work function of the ITO electrode [5], efficient hole injection into Chl *a* is expected, irrespective of the spin state of $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$. Therefore, the observation of emission from ITO suggested that electrons injected from the Al electrode passed through the active layer to the ITO electrode when $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ was in the low-spin state. A model describing the on/off switching of EL emission accompanying the spin transition is as follows. When $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ is in the high-spin state, holes and electrons injected into the active layer recombine at Chl *a* to form excitons, while in the low-spin state, electrons pass through the active layer via $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ to ITO, leading to disappearance of the recombination in Chl *a* (Figure 1).

In this study, to verify the model, we fabricated OLEDs with different structures. We introduced poly(*N*-vinylcarbazole) (PVK) between the ITO electrode and the active layer as a hole transport and electron blocking layer, and used Nile Red (NR) as an emitting material. The EL spectra obtained from each device in the high- and low-temperature regions, where $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ is in the high- and low-spin states, respectively, are reported.

2. Experimental details

The dpp ligand and spin crossover complex $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ were synthesized using the procedures described in the literature [6, 7]. Chl *a* was purchased from Juntec, and NR and PVK were purchased from Tokyo Kasei. All the commercially obtained reagents were used as received. The ITO substrate was cleaned by ultrasonic agitation for 15 min in acetone, 2-propanol, and methanol, prior to film fabrications. A PVK layer with a thickness of 15 nm was fabricated via spin coating using a chloroform solution. The active layer was also fabricated by spin coating using an acetonitrile solution containing $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ and the emitting material (Chl *a* or NR) in 4:1 molar ratio for

[Fe(dpp)₂](BF₄)₂:Chl *a*, and 20:1 molar ratio for [Fe(dpp)₂](BF₄)₂:NR. The acetonitrile solution was filtered through a membrane filter (0.2 μm) before spin coating. The thickness of the active layer film was approximately 50 nm. Light-emitting devices with the structure ITO/PVK/[Fe(dpp)₂](BF₄)₂:Chl *a*/Al and ITO/[Fe(dpp)₂](BF₄)₂:NR/Al were prepared by vacuum deposition of the Al cathode (30 nm) onto the film fabricated on the ITO anode. The base pressure was less than 1×10^{-3} Pa and the deposition rate was ~0.05 nm/s. During deposition, the substrate was maintained at -20 °C to avoid thermal damage to the organic thin films. The emission spectra were measured using a 15 cm monochromator and a nitrogen-cooled back-illumination-type charge coupled device (CCD, Roper Scientific). All devices were held in an Oxford OptistatCF cryostat.

3. Results and Discussion

Figure 2 shows the EL spectra of the ITO/PVK/[Fe(dpp)₂](BF₄)₂:Chl *a*/Al device at 300 and 200 K. EL spectra attributable to Chl *a* were clearly observed even at 200 K. PVK is a hole transporting material and can act as an electron blocking layer [8]. Therefore, in the ITO/PVK/[Fe(dpp)₂](BF₄)₂:Chl *a*/Al device, PVK was capable of preventing

electrons from reaching the ITO electrode, resulting in electron accumulation in the active layer. In this situation, even in the low-temperature region where $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ was in the low-spin state, electron injection into Chl *a* occurred, leading to EL emission.

This result supports the model shown in Figure 1.

To understand the mechanism of EL suppression caused by electron passage through the active layer of the ITO/ $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$:Chl *a*/Al device, we examined whether EL suppression due to the lack of electron injection into the emitting material in the low-temperature region, where $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ was in the low-spin state, occurred, regardless of the type of emitting materials used. Figure 3 shows the EL spectra of an ITO/ $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$:NR/Al device containing 5 mol% NR in the active layer as an emitting material. EL emission was observed to occur even at 200 K, implying that the EL suppression was dependent on the type of emitting material used; the key to EL suppression was a combination of $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ and the emitting material.

It became apparent that electron injection into Chl *a* in the ITO/ $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$:Chl *a*/Al device was regulated by the spin transition of $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$. The regulation can be explained by a shift in the energy level of the molecular orbital concerning electron

transport, as shown in Figure 4. When $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ is in the high-spin state, the energy level of the molecular orbital concerning electron transport should be around or above that of Chl *a* (Figure 4a). Thus electrons can flow into Chl *a*, leading to the generation of excited Chl *a* and to EL emission. On the other hand, when $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ is in the low-spin state, the molecular orbital concerning electron transport might shift to a level below that of Chl *a* (Figure 4b), that is, the molecular orbital level might come close to the work function of the Al cathode. The shift in energy level causes the injected electrons to flow only into $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ and pass through the active layer to the anode via $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$, thus preventing electron injection into Chl *a* and resulting in the disappearance of excited Chl *a*. This mechanism also explains the result observed for the ITO/ $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$:NR/Al device. Because Chl *a* is a hole transport material and its lowest unoccupied molecular orbital (LUMO) level is -2.9 eV (estimated from the reported ionization potential in Ref. 5 and the HOMO-LUMO gap), which is higher than the work function of Al, the electron injection efficiency into Chl *a* is quite likely to be low. On the other hand, the LUMO level of NR is -3.5 eV, which is closer to the work function of Al than is the LUMO level of typical electron transport

materials such as Alq (the LUMO of which is around -3.0 eV). Hence, NR acts as an electron transport material [9, 10]. Therefore, even after the spin transition of $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ accompanying the shift in the energy level concerning electron transport, electron injection into NR occurred as before, and EL emission from NR was observed for both the spin states of $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ (Figure 4c and d).

The most likely origin of the shift in the molecular orbital is a structural transition accompanying the spin transition. The molecular structures of $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ in the high- and low-spin states are different, which is typical in spin crossover complexes [11].

As a result of the molecular structure transition, energy levels of molecular orbitals certainly change, as indicated by the change in the absorption spectra [2]. In addition, it is important to note that $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ is a metal complex. When the spin states of divalent iron complexes change from the high- to the low-spin state, the distance between central iron ion and the nitrogen atom of the ligand in the low-spin state reduces as compared to that in the high-spin state [12]. Such a structural change might cause the injected electrons to be transferred from the π -orbital of the dpp ligand to the d-orbital of iron, which is supported by the observation that CT bands become strong in the low-spin

state [2], and this leads the transferred electrons to pass through the active layer via the d-orbital of iron. In other words, the spin transition may result in the creation of a new electron transport path originated from the d-orbital, in addition to the energy shift mentioned above.

4. Conclusions

By introducing PVK between the ITO electrode and the active layer, we prevented EL quenching in the device consisting of the spin crossover complex $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ and emitting Chl *a*, while the device without PVK showed reproducible on/off switching of EL emission accompanying the spin transition of $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$. Because PVK acts as the hole transport and electron blocking layer, suppression of the EL quenching indicates that the quenching is dominated by the efficiency of electron injection into Chl *a*. We also fabricated an EL device composed of ITO/ $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$:NR/Al, in which the emitting material NR acts as the electron transporting material with its low LUMO level. In this device, we observed EL emission from NR, irrespective of the spin state of $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$. These results reveal that EL quenching accompanying the spin

transition depends on the change in the molecular orbital level concerning electron transport of $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$.

In addition to the drastic change in magnetic properties, the change in the molecular orbital level of spin crossover complexes is a prospective tool for controlling the characteristics of other organic thin film devices such as photovoltaic cells, field-effect transistors, and spintronics devices.

Acknowledgements

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Figure 1. A model for the reproducible EL on/off switching of Chl *a* accompanying the spin transition of $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$.

Figure 2. EL spectra for the ITO/PVK/ $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$:Chl *a*/Al device at 300 and 200 K.

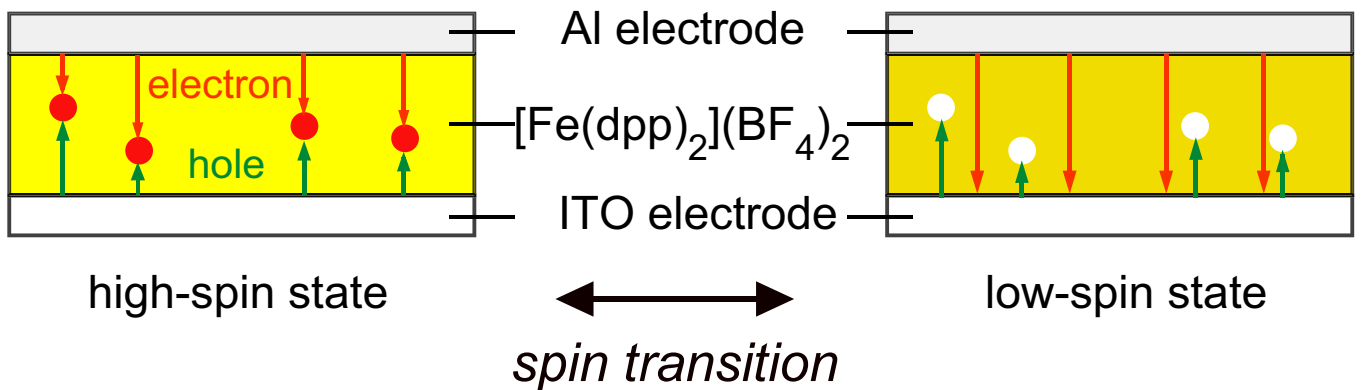
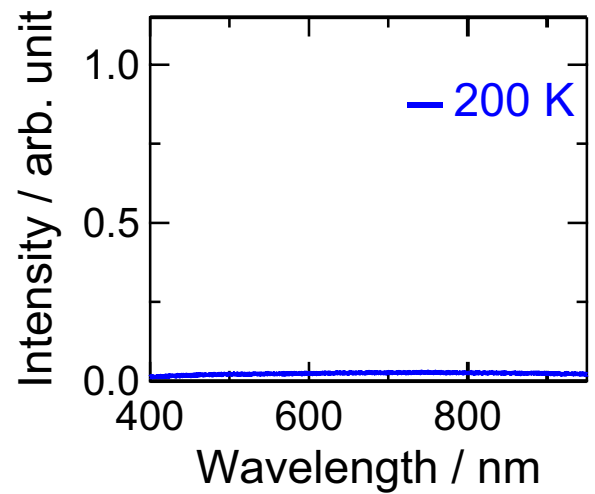
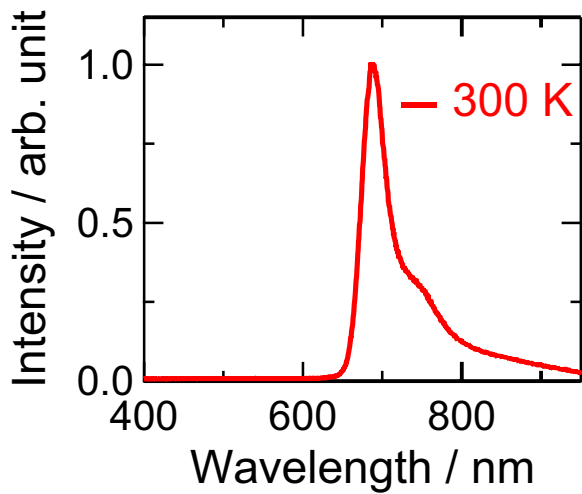
Figure 3. EL spectra for the ITO/ $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$:NR/Al device at 300 and 200 K.

Figure 4. Schematic representation of the mechanism of the EL on/off switching based on the energy level diagram. (a) Chl *a*-doped device with $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ in its high-spin state, (b) Chl *a*-doped device with $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ in its low-spin state, (c) NR-doped device with $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ in its high-spin state, and (d) NR-doped device with $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ in its low-spin state. The energy level change in the molecular orbital concerning electron transport accompanying the spin transition regulates electron

injection into Chl *a*, but does not affect the electron injection into NR because of its low LUMO level.

Figures 1

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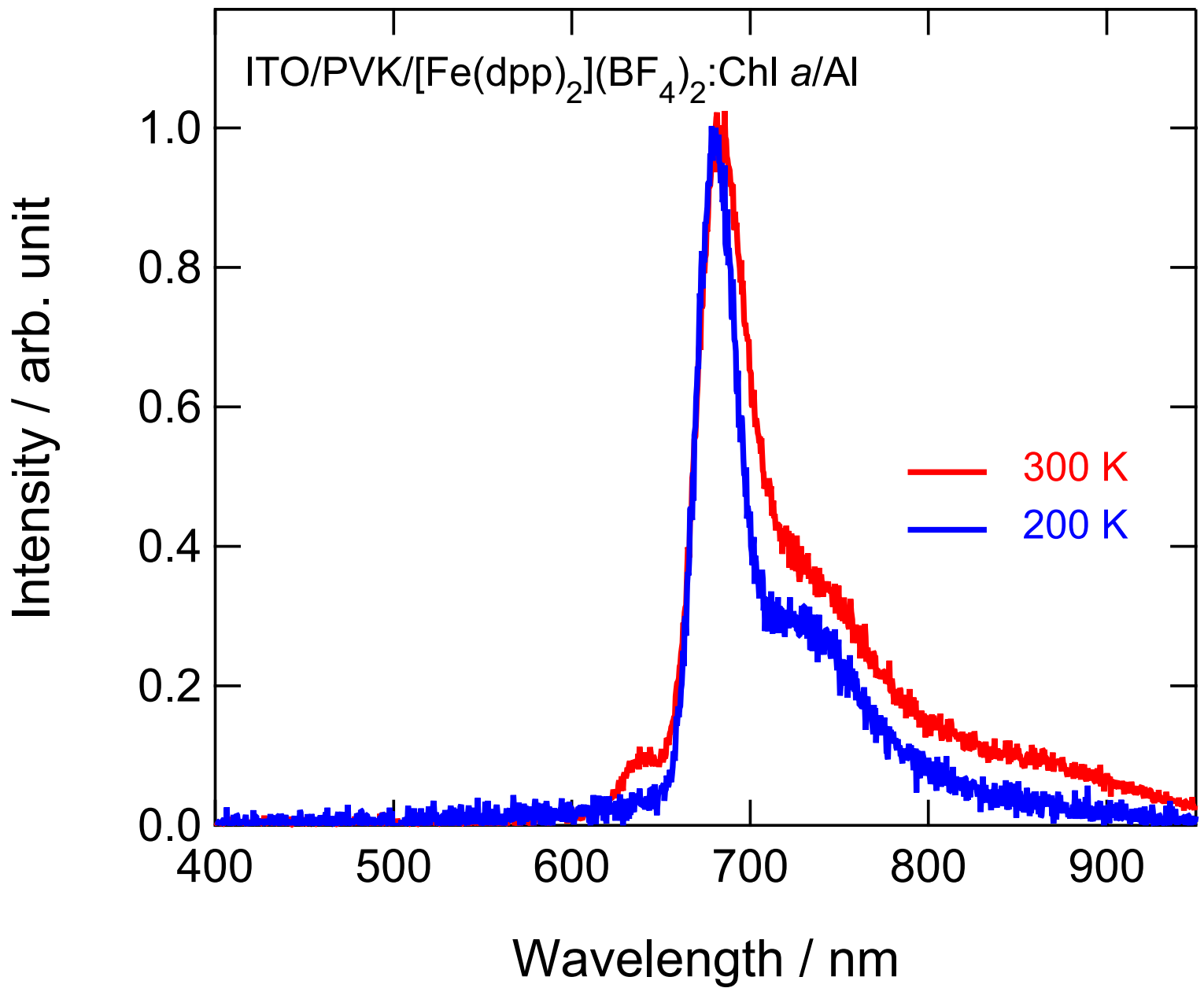


● Chl a in the *emitting state*

○ Chl a in the *non-emitting state*

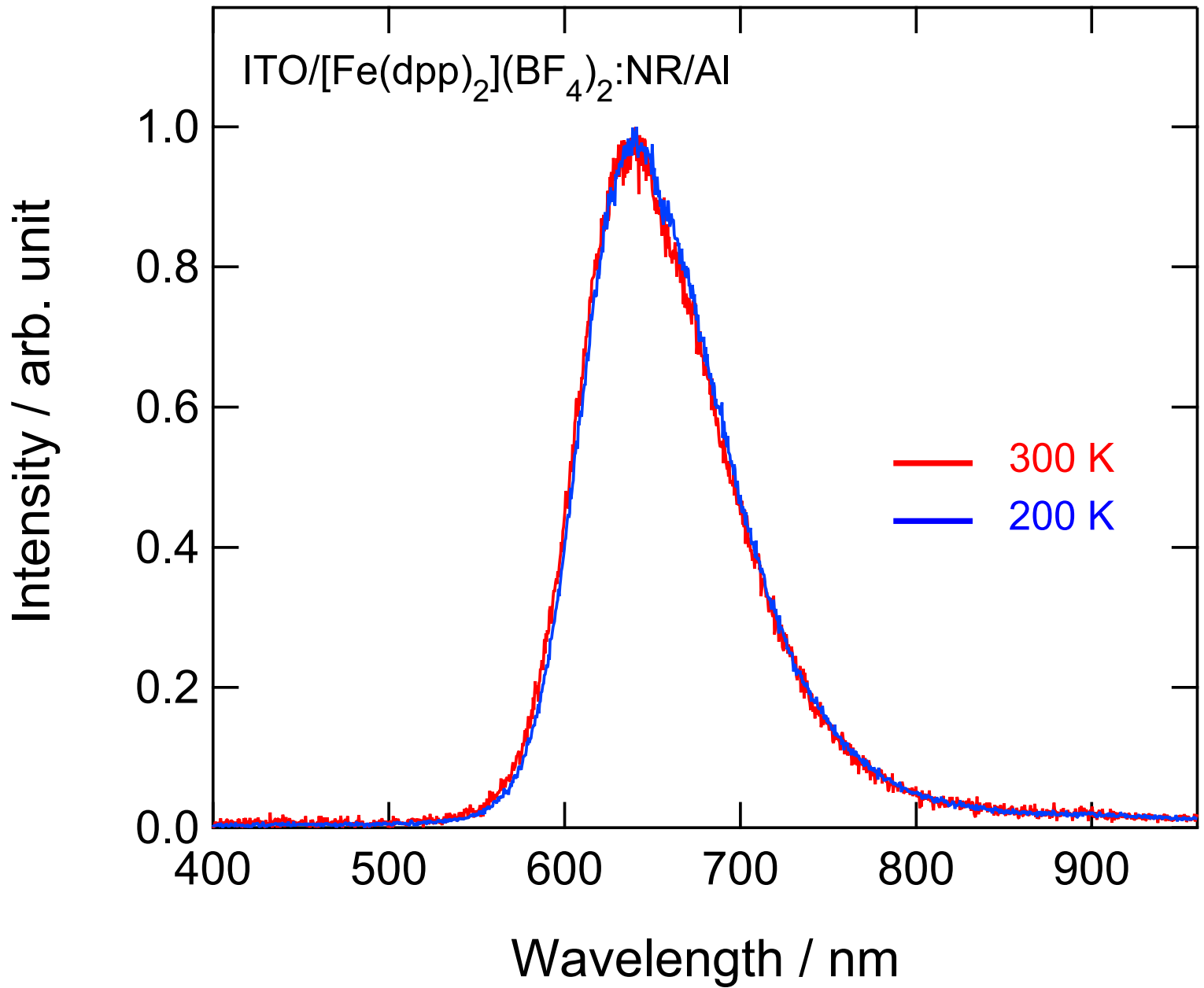
Figures 2

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