# The Electroluminescence Spectrum of Chlorophyll *a*

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We fabricated organic-light-emitting diode (OLED) from chlorophyll *a*, and measured electroluminescence (EL) and photoluminescence (PL) spectra. The EL spectrum exhibits a peak at 700 nm and a shoulder at 750 nm, while the PL spectrum exhibits a peak at 750 nm. The external quantum efficiency of the fabricated OLED linearly increases for the applied voltage above $V = 4$ V and reaches to $9 \times 10^{-8}$ at $V = 8$ V.

The thin-film organic light-emitting diode (OLED) was fabricated by Vincett et al. for the first time.[1] In this device, light emission occurs through the recombination process of electron–hole pairs injected from electrodes (electroluminescence = EL). Based on this principle, most of the EL studies intend to produce devices with various colors and with high efficiencies. The fabricated devices are equipped with electron- and hole-transport layers and sometimes with multi-emission layers. The EL spectra as well as quantum efficiencies are no more the intrinsic properties of materials in these devices. On the other hand, the EL-device technique is a new spectroscopy of potential use for insulating materials. For this purpose, the transport layers are rather inconvenient and the OLED having a structure of metal/insulator/metal junction is better to study. However, such EL studies are quite few at present.

We recently succeeded in obtaining the EL spectra of heme proteins (cytochrome *c* and myoglobin) by fabricating the ITO/protein/Al junctions.[2,3] This is the first report on the biomolecular light-emitting diode (BIODE). Although the reproducibility of the data is quite poor for the current and EL intensity, the quantum efficiency evaluated from the two quantities is reproducible for all the fabricated samples within 20% error. Interestingly, the heme proteins do not or hardly exhibit photoluminescence (PL). Such difference between EL and PL has not been reported yet.[4]

In this letter, we report the EL spectrum of chlorophyll *a* (Chl *a*), a well-known compound for photosynthesis.[5] Figure 1 shows the molecular structure of Chl *a*. This molecule has a porphyrin skeleton similar to heme, incorporating $Mg^{2+}$ with closed shell. The EL spectrum is not reported for Chl *a*, although the PL spectrum is reported.[6,7] The Chl-*a* molecules tend to aggregate in polar solvents.[6] Upon the aggregation, both absorption and PL spectra exhibit red shift.[6]

Figure 2a illustrates a schematic view of the ITO/Chl *a*/Al junction prepared for BIODE in this study. The effective size of the junction was $1.5 \times 1.5\,\mathrm{mm}^2$. High-purified Chl *a* (>99%; from spirulina) was purchased from Juntec Co. A film was fabricated from the chloroform solution of Chl *a* (0.45 wt %) by the spin-coating technique. The Al electrode was formed on the Chl-*a* film by the vacuum evaporation technique. Figure 2b shows a AFM image of a Chl-*a* film fabricated on an ITO electrode. The thickness and the roughness of the fabricated film were approximately 60 and 2 nm, respectively.

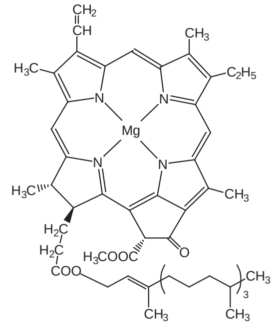

**Figure 1.** The molecular structure of chlorophyll *a* (Chl *a*).

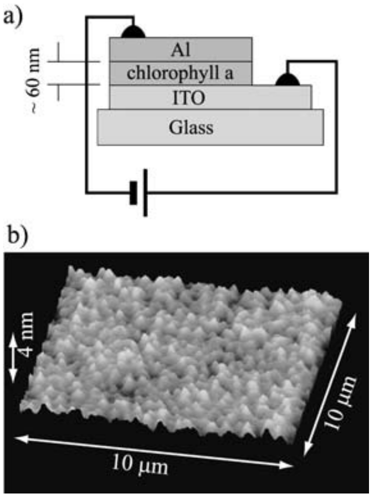

**Figure 2.** (a) A schematic view of chlorophyll *a* BIODE. (b) The AFM image of a Chl-*a* film fabricated on an ITO electrode.

The current–voltage and EL intensity–voltage characteristics were measured by applying the negative voltages to an Al electrode and positive voltages to an ITO electrode. When a bias voltage was inversely applied, the fabricated devices were quickly damaged. Figures 3a and 3b show the two characteristics simultaneously measured. No hysteretic behavior was observed in these characteristics. This contrasts with the case of ITO/cytochrome *c*/Al BIODE. The voltage dependence of the external quantum efficiency, shown in Figure 3c, was evaluated from the two characteristics. The quantum efficiency linearly increases above $V = 4$ V and reaches to $9 \times 10^{-8}$ at $V = 8$ V. This result is consistent with other samples within 20% error. The efficiency of chlorophyll-*a* BIODE is a little higher than that of cytochrome-*c* BIODE (Q.E. = $6–8 \times 10^{-8}$ at $V = 13$ V) but extremely smaller than that of OLED devices studied for practical purpose. This is due to a single-organic-layer structure of the

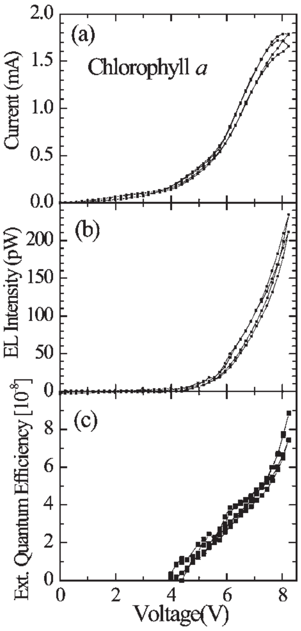

**Figure 3.** (a) The current–voltage and (b) the EL intensity–voltage characteristics of Chl-*a* BIODE. (c) The external quantum efficiency evaluated from (a) and (b).

fabricated OLED. In this type of OLED, injected holes and electrons do not balance, resulting the low efficiency of the exciton formation. By forming appropriate electron- and hole-transport layers, the quantum efficiency should be increased.

The EL and PL spectra were measured using a 15 cm monochromator and a liquid-nitrogen-cooled back-illumination-type CCD detector. Figure 4 shows the EL, PL, and absorption spectra of a Chl-*a* film fabricated in this study. A monomeric Chl *a* exhibits an absorption peak around 670 nm (Q band).[6,7] The corresponding peak appears at 750 nm in the aggregated form of Chl *a*.[6] The absorption spectrum of the film prepared in this study exhibits a broad band peaked around 670 nm, having a tail in the longer-wavelength region. This suggests that the film fabricated in this study is a mixture of aggregations and monomers of Chl *a*. The oscillator strength of the Q-band for monomeric and aggregated Chl *a* are approximately the same in the solutions.[6] If we assume the absorption spectra of Chl *a* in films and in solutions are the same, we can roughly estimate that 10–20% of Chl *a* molecules are aggregated in the film from the observed spectrum.

The PL spectrum shows a peak at 750 nm. This spectrum is consistent with that reported for aggregated Chl *a*,[6] although most of Chl *a* molecules in the films are expected to be in a monomeric form. This can be explained by assuming the non radiative energy-transfer process where excitons formed in the monomer site hops to the aggregated segments with smaller exciton energy through the near-field dipole–dipole interaction (Föster transfer process).

Contrary to the PL spectrum, the EL spectrum exhibits a peak at 700 nm and a shoulder at 750 nm. Since the shoulder at 750 nm is consistent with the peak in the PL spectrum, we concluded that a new peak appear at 700 nm in the EL spectrum.

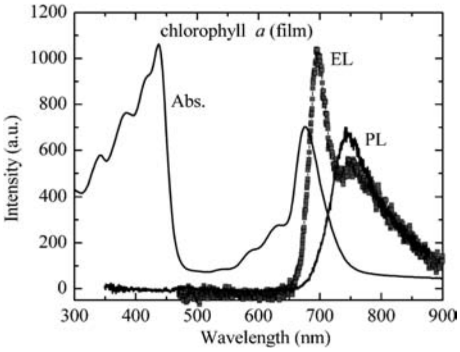

**Figure 4.** The EL, PL, and absorption spectra of the Chl-*a* films fabricated in this study. Note that the peak at 700 nm in the EL spectrum does not appear in the PL spectrum.

In the case of the PL spectrum, the excitation process is limited by an optical-selection rule. Such a selection rule does not exist in the EL-excitation process. Meanwhile, EL excitation process is affected by the differences of energy levels between molecular orbitals and electrodes (Fermi level). Thus the EL spectrum of some compound is not always similar to the PL spectrum of the same compound, especially if the compound has complicated electronic structure. Although detailed assignment of the EL spectrum obtained in this study is still difficult at the present stage, the observed difference suggests that the character of the 700 nm band is different from that of the 750 nm band. More detailed studies are necessary in order to assign the two transitions explicitly.

In conclusion, we have measured the PL, EL, and absorption spectra of the Chl-*a* films. This is the first report on the EL spectrum of Chl *a*. The PL spectrum exhibits a band typical for the aggregated Chl *a* at 750 nm. The EL spectrum exhibits a strong peak at 700 nm in addition to a shoulder at 750 nm. The external quantum efficiency of the fabricated EL device linearly increases for the applied voltages above 4 V, and reaches to $9 \times 10^{-8}$ at $V = 8$ V.

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