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Light-emitting diodes fabricated from biomolecular compounds

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Abstract

We fabricated ITO/biomolecule/Al junctions using chrolophyll *a*, cytochrome *c*, myoglobin, hemin, Vitamin B_{12}. All the junctions worked as organic light-emitting diode (OLED). The quantum efficiencies of the fabricated OLED were of the order of 1×10^{-7} around $V = 10$ V, and did not seriously depend on whether or not a compound exhibits photoluminescence. Based on the energy diagram of the ITO/cytochrome *c*/Al junction, we discuss the difference of the EL spectrum from the photoluminescence or absorption spectrum.

Keywords: Biomolecule; BIODE; OLED; Electroluminescence; Molecular device; Chlorophyll *a*; Cytochrome *c*; Myoglobin; Hemin; Vitamin B_{12}

1. Introduction

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 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 not always necessary and the OLED with simple metal/insulator/metal junction has some advantage. However, such EL studies are quite few at present.

We recently succeeded in obtaining the EL spectra using biomolecules [2,3]. This is the first reports on the biomolecular light-emitting diode (BIODE). Some of the biomolecules studied do not or hardly exhibit photoluminescence (PL), but exhibit EL. In this respect, the gap between the EL and PL properties is an interesting problem not only for bioscience but also for physics. In this paper, we review our EL studies on biomolecules, and present a model which well explains the difference between the EL and PL properties in heme proteins.

2. Results

2.1. Chlorophyll a

Chlorophyll *a* is a well-known compound for photosynthesis [4]. The inset of Fig. 1 shows the molecular structure of chlorophyll *a*. This molecule has a porphyrin skeleton similar to heme, incorporating Mg^{2+} with closed shell. The chlorophyll *a* molecules tend to aggregate in polar solvents. Upon the aggregation, both absorption and PL spectra exhibit red shift [5].

Fig. 1(a and b) shows the current–voltage and EL intensity-voltage characteristics simultaneously measured by applying the negative voltages to an Al electrode and positive voltages to an ITO electrode [3]. When a bias voltage was inversely applied, the fabricated devices were quickly damaged. The voltage dependence of the external quantum efficiency, shown in Fig. 1c, was evaluated from the two characteristics. The quantum efficiency almost linearly increases above $V = 4$ V and reaches to 9×10^{-8} at $V = 8$ V. This quantum efficiency is extremely smaller than that of OLED devices studied for practical purpose. This is due to a single-organic-layer structure of the 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.

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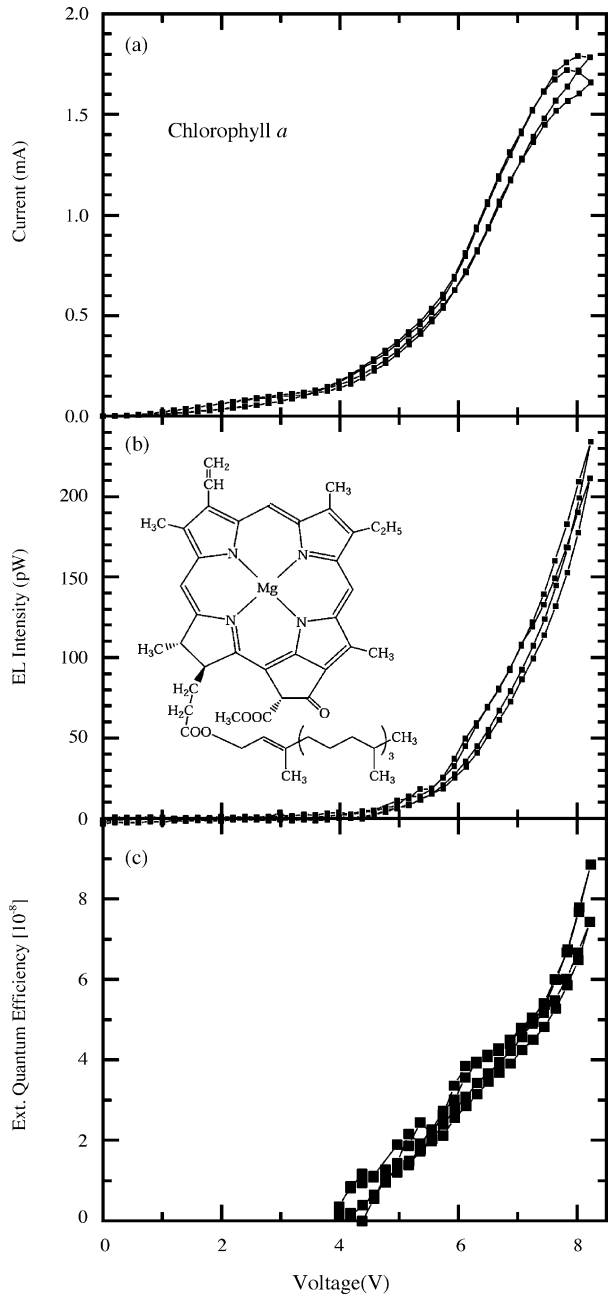

Fig. 1. (a) The current-voltage and (b) the EL intensity-voltage characteristics of chlorophyll *a* BIODE. (c) The external quantum efficiency evaluated from (a) and (b). The inset in (b) shows the molecular structure of chlorophyll *a*.

The EL and PL spectra were measured using a 15 cm monochromator and a liquid-nitrogen-cooled back-illumination-type CCD detector. Fig. 2 shows the EL, PL, and absorption spectra of a chlorophyll *a* film fabricated in this study [3]. A monomeric chlorophyll *a* exhibits an absorption peak around 670 nm (Q band) [5]. The corresponding peak appears at 750 nm in the aggregated form of chlorophyll *a* [5]. 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 main component of the film fabricated in this study is chlorophyll *a* monomers. The PL spectrum shows a peak at 750 nm. This spectrum is consistent with that reported

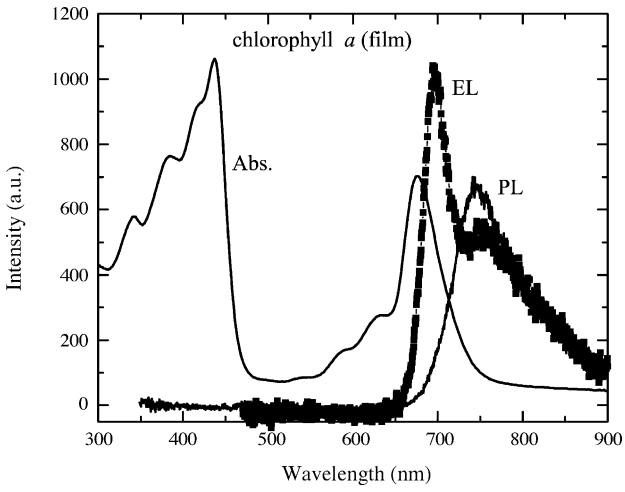

Fig. 2. The EL, PL, and absorption spectra of the chlorophyll *a* films fabricated in this study. Note that the peak at 700 nm in the EL spectrum does not appear in the PL spectrum.

for aggregated chlorophyll *a* [5], although most of chlorophyll *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 (Förster transfer process). 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 appears at 700 nm in the EL spectrum. Although detailed assignments on the EL spectrum are 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.

2.2. Cytochrome *c*

Cytochrome *c* is relatively low-molecular-weight protein, which functions as an electron carrier in the living systems [4]. This compound contains heme (iron porphyrin) in the low-spin state. Contrary to chlorophyll *a*, cytochrome *c* hardly exhibit PL. Fig. 3 shows the EL spectrum of ITO/cytochrome *c*/Al junction and absorption spectrum of cytochrome *c* film [2]. The EL spectrum is quite broad in contrast with the EL spectrum of chlorophyll *a*. The two peaks around 410 and 530 nm are consistent with the absorption band, and attributable to Soret and Q bands (π–π transitions). In addition to these peaks, the EL spectrum exhibits a broad band around 670 nm attributable to ligand-metal charge-transfer (LMCT) transition. Although this band also appears in the absorption spectrum, the absorption intensity of the band is much weaker than that of Soret or Q bands. The quantum efficiency of cytochrome *c* BIODE almost linearly increases for the applied voltages above 6.5 V and reaches to 6–8 $\times 10^{-8}$ at $V = 13$ V. This value is comparable to the quantum efficiency of chlorophyll *a* BIODE.

2.3. Myoglobin

Myoglobin works for the transport and storage of oxygen in the living system [4]. There are no PL studies reported for this