Electroluminescence of a J-Aggregated Cyanine Dye Multilayer

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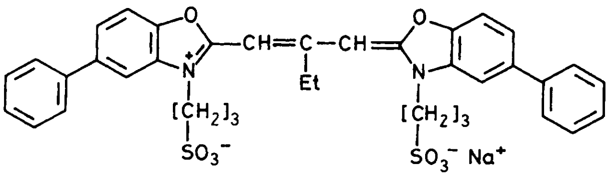
Electroluminescence was observed from the multilayer films of a cyanine dye which exhibited sharp and intense fluorescence due to J-aggregation.

J-Aggregated dyes, in which the dye molecules have a head-to-tail orientation, exhibit a sharp and intense absorption band, which shows a red-shift from the band of monomer absorption observed in highly diluted solutions. They also show resonance fluorescence. If multilayer films of J-aggregated dyes can be prepared, large photoconductivity and intense electroluminescence in thin organic films may be realized. In fact, Sugi *et al.* have observed the photocurrent spectrum due to the J-like aggregation in dye-sensitized Langmuir–Blodgett (LB) films.[1] Since photo-emission from J-aggregated cyanine dyes is reported to be very efficient,[2] and since materials with high fluorescence efficiency are con-



(1)

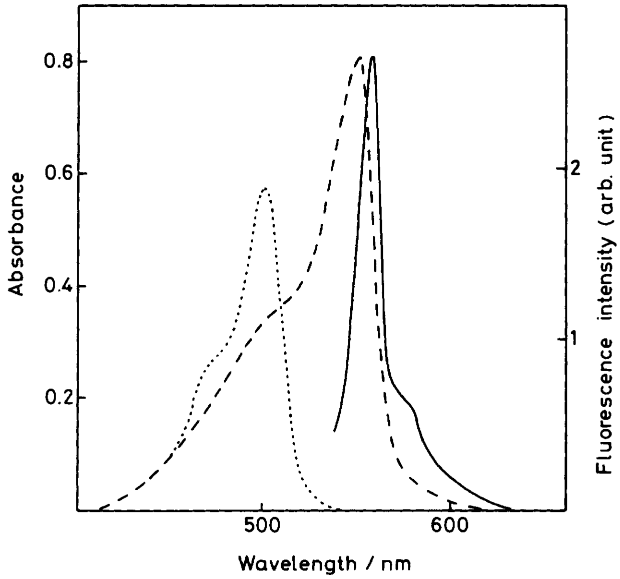


Figure 1. Absorption (broken line) and fluorescence (solid line) spectra of multi-layered cyanine dye (**1**). The absorption spectrum of (**1**) in methanol (0.4×10^{-5} M) is also shown (dotted line).

sidered to be the best candidates for the realization of highly-efficient electroluminescence, we performed a study of the electroluminescence from a J-aggregated cyanine dye.

A monolayer of the cyanine dye (**1**) was spread from a 10^{-3} M chloroform solution on a subphase which contained 10^{-5} M Al^{3+} ions; a surface pressure of 30 mN m^{-2} was applied. We were not able to transfer the monolayer onto substrates by the usual LB method, but the horizontal lifting technique was successful.[3] The absorbance at 550 nm of the multilayer increased linearly with the number of repeated collections, indicating regular stacking of the monolayers. Thus, the multilayers were assumed to be stable Z-type films. The metal/multilayer/metal sandwich cells were prepared as follows. The multilayers were collected on Al-coated glass substrates and Au was vacuum evaporated on the multilayers to form rectangular-top electrodes with 0.1 cm^2 area. The transmittance of the Au electrodes was about 50%, and that of the Al electrodes *ca.* 30%. The emission, when AC or DC voltage was applied, was detected with a photomultiplier and observed directly on an oscilloscope. Electroluminescence spectra were measured using a 10 cm monochromator and a photon counter. These measurements were performed under a helium atmosphere after the multilayer cells were dried *in vacuo* (10^{-3} Torr, 1 h).

Figure 1 shows the absorption spectrum of the multilayer (30 layers on a glass substrate). The absorption band is intense and sharp and located at 550 nm, which is 46 nm longer than the band of the monomer absorption. The fluorescence spectrum of the multilayer is also shown. Its bandwidth is narrow and the Stokes shift very small. These optical properties clearly demonstrate that the cyanine dyes form J-like aggregates.

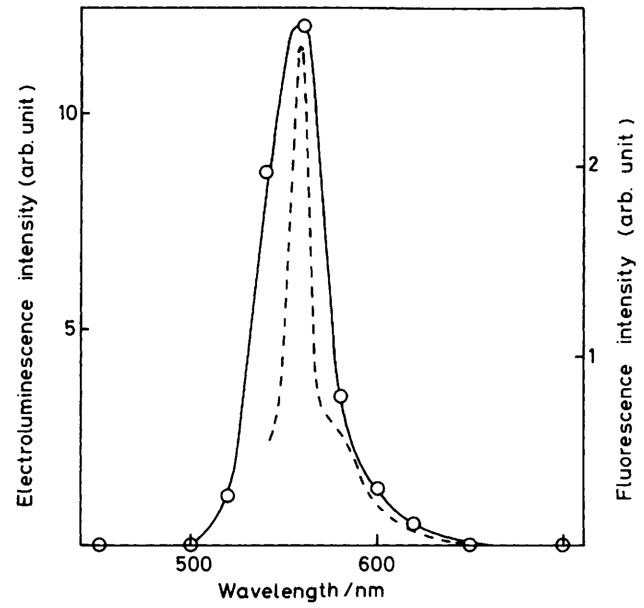


Figure 2. Electroluminescence spectrum in the Au/multilayer (30 layers)/Al cell, applied AC voltage (60 Hz) = 7 V. The broken line shows the fluorescence spectrum of the multilayer (30 layers).

Electroluminescence from the multilayer was observed when AC or DC voltage was applied to the sandwich cells. The yellow emission was seen with the naked eye in a dark room, when AC voltage (60 Hz) higher than 4 V was applied to the cell with 30 layers. The threshold voltage was increased to 8 V when the 60-layer cell was used. The emission occurred only when the Au electrode was biased positive.

The indium–tin oxide (I.T.O.)/multilayer (30 layers)/Al cell was examined as well; the emission was also observed when the I.T.O. electrode was biased positive. These observations suggest that the electroluminescence was caused by an injection of carriers; namely, holes were injected from the Au or I.T.O. electrode.

The electroluminescence spectrum shown in Figure 2 corresponds well with the fluorescence spectrum (broken line). This proves that electroluminescence originates from the cyanine dyes having J-like aggregation.

Roberts *et al.* reported that the electroluminescence from the LB films of anthracene derivatives was due to excimer-like structures.[4] To our knowledge, electroluminescence originating from molecular aggregates is unprecedented. Our findings may be valuable since the aggregated structures of dyes that dominate efficiency and the wavelength of emission are controllable in a variety of ways.

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