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### Effect of Electric Field on Fluorescence of Phthalocyanine Thin Films

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## **Effect of Electric Field on Fluorescence of Phthalocyanine Thin Films**

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Results are presented of a study on luminescence quenching, by an applied electric field, of x-form metal-free phthalocyanine and type II chlorogallium phthalocyanine, both of which are highly efficient photocarrier generating material. Experimental results, especially the time dependence, indicate that the quenching of the fluorescence seems to be the effect of photogenerated charges, rather than induced by an electric field. An irreversible decrease of the fluorescence intensity occurs under prolonged illumination with electric field applied.

**Keywords:** fluorescence quenching; phthalocyanines

### **INTRODUCTION**

Phthalocyanines (Pc's) are photoconductive and are being used as photoactive materials in photocopiers and laser printers. Triggered by the recent discovery of highly sensitive modifications such as titanyl phthalocyanine and gallium phthalocyanines there is a renewed interest in the factors controlling the photosensitivity in this class of materials. Results of electroabsorption studies indicate that charge-transfer (CT) states play an important role in the generation of charge carriers [1-3]. A question arises: Can the emission of these materials also be modulated by an electric field? Fluorescence is expected to be sensitive to the external electric field if the separation of positive and negative charges competes with radiative decay.

Fluorescence of Pc's has been reported to be indeed sensitive to an electric field: it can be quenched by applying an electric field. Popovic studied the field effects on the intensity of the fluorescence of Pc films and concluded that singlet excited state goes over, assisted by an electric field, to a CT state which dissociate into charge carriers [4]. The model implies that the final state of the optical absorption is a nonpolar excited state and that the CT state is assumed to be generated in the course of the succeeding relaxation. Results of electroabsorption measurement, on the other hand, indicate that the final state of the optical transition itself is polar, presumably has a character of a CT state.

Here we present the results of our study on fluorescence quenching of two highly sensitive photocarrier generating material, x-form metal-free phthalocyanine and chlorogallium phthalocyanine (type II). A recent picosecond study has revealed that amplitudes, as well as lifetimes, can be modulated [5].

## EXPERIMENTAL

Pc's in their specific crystal modifications were a gift from Fuji-Xerox Co. Ltd. (for their preparation see Reference 3). They were in the form of fine particles ( $0.2\ \mu\text{m}$  in diameter) dispersed in a polymer (polyvinyl butylal) matrix. Thin ( $0.2\ \mu\text{m}$ ) films were prepared on tin oxide-coated glass plates by dip-coating, as shown in Fig. 1(a). A blocking layer ( $5\ \mu\text{m}$ ) of N-(methoxymethyl)-nylon was coated on the tin oxide layer before a Pc layer was prepared. A HeNe laser (1 mW at 632.8 nm) or a laser diode (8 mW at 635 nm) was used as the exciting light source. Fluorescence from the sample specimen was collected with a spherical mirror and was focused onto the entrance slit of a monochromator (Bausch & Lomb, High Intensity) and was detected with a NIR-sensitive photomultiplier (Hamamatsu, R-2658). A solution filter of malachite green was placed before the entrance slit of the monochromator in order to reject the scattered excitation light. Square wave voltage from a signal generator was amplified by a bipolar amplifier and was applied to the sample.

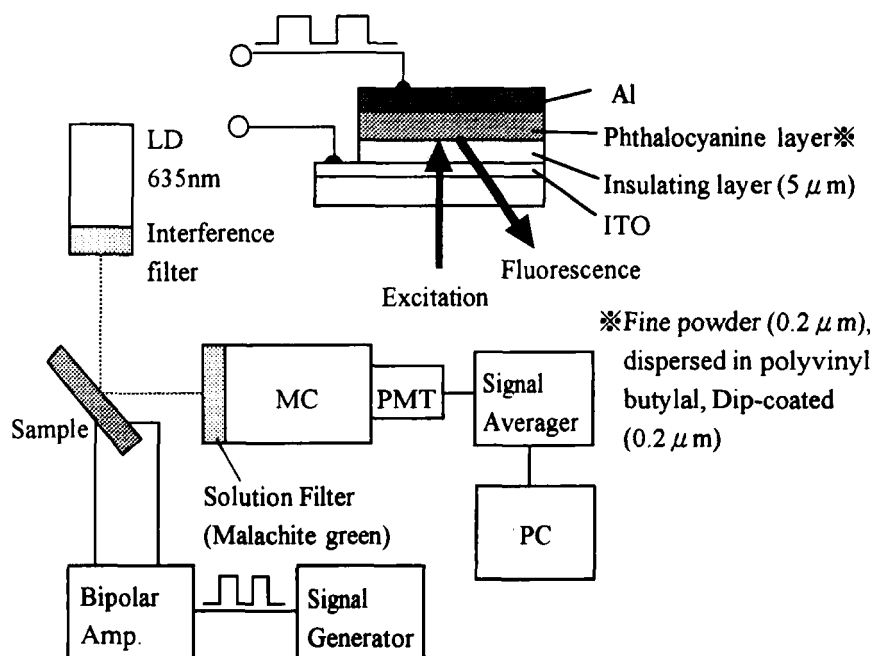


FIGURE 1 Arrangement for fluorescence measurements. Insert shows the sample configuration.

## RESULTS

When a square wave voltage was applied the fluorescence intensity decreased. The quenching was, however, not instantaneous. Figure 2 shows the temporal behavior of the quenching. On applying an electric field the fluorescence initially decreases by several percent in tens of a millisecond. After this relatively fast decrease the intensity continued to fall, but with a reduced rate (Fig.2). When the applied field is removed the fluorescence recovered. However, after prolonged application of a voltage, some part of the quenching remained. What is remarkable is that this decrease in the fluorescence intensity occurred only when both an electric field and illumination were present.

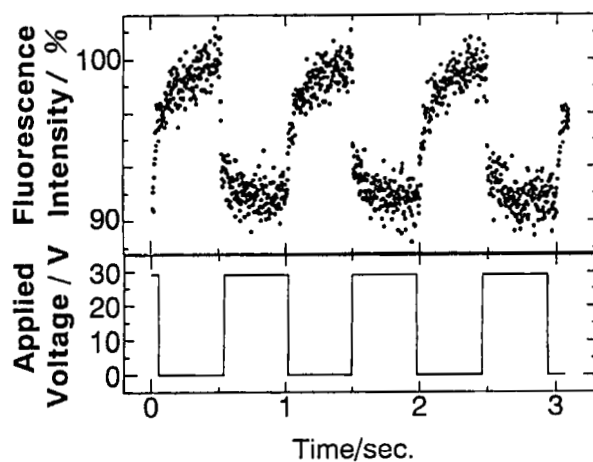


FIGURE 2 Temporal behaviour of the fluorescence quenching. As time goes on the progress of quenching becomes slower.

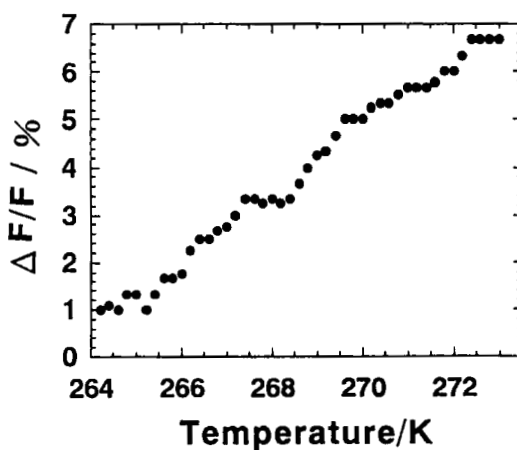


FIGURE 3 Temperature dependence of fluorescence quenching. (a) The quenching becomes slower at lower temperatures. (b) Quenching observed 0.5 s after an electric field of  $6 \times 10^4$  V/cm is applied.

The quenching of the fluorescence became slower when the temperature was lowered (Fig. 3). It practically disappeared below 265 K.

With the electrode arrangement shown in Fig. 1 both photocurrent and fluorescence could be monitored. The insulating layer of nylon had a finite resistivity and a current on the order of  $10^{-7}$  A was observed to flow when a voltage of 30 V was applied. The current, both dark and photo-, was asymmetric when the sign of the electric field was reversed. It was larger when the illuminated side was positively biased.

## DISCUSSION

The time evolution of the quenching in the time scale of milliseconds to hundreds of seconds clearly indicates that during irradiation something is accumulating which quenches the luminescent excited state. The decays of the fluorescence, excited with a picosecond laser, were not single exponential. The main component, however, was characterized by a time constant of 20 ps (in the case of ClGaPc type II). The rate equation for the fluorescent state S is given by

$$d[S]/dt = (1/\tau + k_Q)[S]. \quad (1)$$

If the ion radical of Pc is an efficient energy acceptor for the excited state of Pc,  $k_Q$  should be given by

$$k_Q = \gamma_{SD}[D] \quad (2)$$

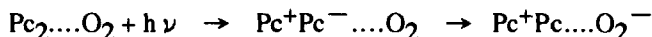
where D stands for the ion radical. The upper limit for the density of charge [D] injected from the electrode, estimated by [6]

$$[D] = V/4\pi \epsilon \epsilon_0 d^2, \quad (3)$$

is  $10^{13} \text{ cm}^{-3}$  for  $V = 30 \text{ V}$ ,  $\epsilon = 3$  and  $d = 10 \text{ } \mu\text{m}$ . Considering reported values of  $\gamma_{SD} = 10^{-7} \text{ cm}^3 \text{ s}^{-1}$  [7], this concentration of charges injected from the electrode is several orders of magnitude smaller in order to account for the quenching observed.

It has been recognized that phthalocyanines (Pc's) are a p-type semiconductor. Oxygen is a likely candidate for electron acceptor.

The Pc's studied have a distinct structural feature in common, i.e., they form a lattice in which Pc molecules are arranged in pairs [3], or, in the case of x-form H<sub>2</sub>Pc, in an one-dimensional array [8]. If an oxygen molecule exists close to a Pc pair, separation of charges may be favoured [9].



Pc<sup>+</sup> thus produced is a hole, but can also function as an energy sink.

Experimental observation that optical excitation alone does not deteriorate the luminescent properties of Pc's seems to indicate that the recombination is fast and that the separation of charges is field-assisted.

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- [9] The crystal modifications studied here could only be prepared by treatments including milling in a solvent (see Reference 3) and the crystal structure was deemed unstable against heat treatment or vacuum evaporation. Accordingly no attempt was made to remove oxygen which must be present in the crystal. Simple evacuation at room temperature did not affect the fluorescence characteristics appreciably.