# Drastic Photoluminescence Quenching of Perylene Derivative Membrane with Phthalocyanine Coating

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The photoluminescent property of a bilayer of phthalocyanine and a perylene derivative, a part of an organic photovoltaic cell, was investigated. The monolayer of the perylene derivative exhibited photoluminescence at 824 nm with lifetimes of 1.6 ns and 0.10 ns. The steady state and time-resolved photoluminescence of the 100-nm perylene derivative layer were efficiently quenched with a 100-nm phthalocyanine coating. The high efficiency of the quenching was explained by the high mobility of the photogenerated carrier in the n-type semiconducting perylene derivative, and agreed with the insensitivity of the photovoltaic property of the bilayer to the thickness.

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Recently, remarkable progress has been made in the application of organic semiconductors along with their deep understanding. A perylene derivative shown in Figure 1 exhibits excellent n-type semiconducting characteristics, and has been utilized for significant applications such as photovoltaic cells, high-efficiency photo-detecting devices, etc.[1–10] Our group is developing functional materials for laser fusion targets,[11–13] for which phototunable reflectivity is desirable to achieve one of the crucial requirements for ignition, i.e., a high density compression of the fuel. We have been investigating tuning of the reflection using the photogenerated carrier in the perylene derivative.[13] In the detailed study of the mechanism for understanding the reflection tuning, the photoluminescent properties of the material such as the photoluminescence wavelength and lifetime are determined through their electronic structure.[14,15] If a system contains a luminescent probe molecule in itself, the photoluminescence can be obtained without perturbation by the doped probe. The perylene derivative behaves as a photoluminescent probe in the perylene/phthalocyanine photovoltaic cell. In this paper, we report a drastic quenching of the photoluminescence of the perylene derivative, which is one part of the highly efficient and well-characterized photovoltaic cell.

The perylene derivative denoted as PV (Figure 1) was prepared and purified by a previously reported method.[16] 29H,31H-Phthalocyanine ($H_2Pc$) was purchased from ACROS Inc., and purified by sublimation at 440 °C. The samples of PV/glass, $H_2Pc$/glass, and PV/$H_2Pc$/glass (denoted as PV, $H_2Pc$, and PV/$H_2Pc$, respectively) were prepared by vapor deposition on a non-fluorescent glass plate with non-parallel faces.

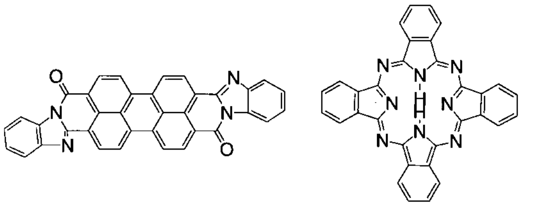

**Figure 1.** Perylene derivative (PV) and phthalocyanine ($H_2Pc$) structures.

For the photoluminescence measurements, the irradiation of the front surface of the film was done using 550-nm monochromatic light at a 40 degree incident angle, and the photoluminescence was monitored from the 50-degree reflection angle to minimize the scattering excitation light. The photoluminescence decay was measured by a time-correlated single photon counting apparatus (Hitachi-Horiba NAES-550) equipped with a 10-atm nitrogen lamp; the photoluminescence was monitored through a cutoff filter (Toshiba O-58) to minimize the scattering.

The visible absorption and the photoluminescence spectra of a 100-nm PV film and an $H_2Pc$ film are shown in Figure 2. The absorption spectra are identical to those reported earlier,[1, 4] whose absorption coefficients indicated the thickness of the present film (100 nm). The photoluminescence spectrum of the PV film had a maximum at 824 nm, the same as that reported by Popovic et al.[1], while photoluminescence of the $H_2Pc$ film was not observed.

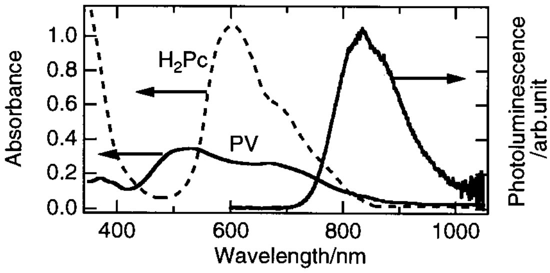

**Figure 2.** Absorption spectra of the 100-nm PV and $H_2Pc$ films, and photoluminescence spectra of the 100-nm PV film.

The photoluminescence decay of the 100-nm PV film is shown in Figure 3(a). It did not show a single exponential decay, but the curves could be satisfactorily analyzed with a double exponential decay (eq (1)) by the deconvolution method using the program equipped with the single photon counting apparatus.[15]

$$I(t) = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2) \quad (A_1 + A_2 = 1) \qquad (1)$$

where I(t) is the ideal decay of the photoluminescence without deconvolution at time t [s], $\tau_1$ (0.10 ns) and $\tau_2$ (1.6 ns) are lifetimes of the photoluminescence, and $A_1$ (0.983) and $A_2$ (0.017) are the corresponding pre-exponential factors. The relative photoluminescence yield of each component was estimated to be $\Phi_1$ = 0.80 and $\Phi_2$ = 0.20, using the following equation.

$$\Phi_n = A_n\tau_n/(A_1\tau_1 + A_2\tau_2) \qquad (2)$$

A value similar to the major and shorter lifetime ($\tau_1$) was found in the previous report by Biglov et al.[5] to be the longer lifetime value (80 ps), while the present minor but not negligible component ($\tau_2$ =1.6 ns and $\Phi_2$ =0.20) was not observed in the previous report. Because the time region of the present experiment (25 ns) was longer than that in the previous report (~ 500 ps), the

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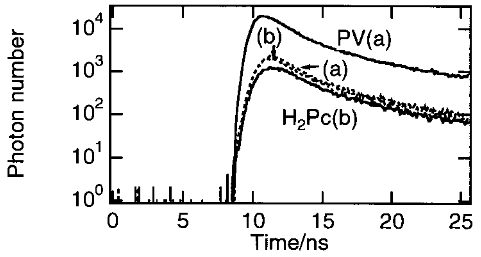

**Figure 3.** Fluorescence decays of the PV monolayer (100 nm) (a), and the bilayer of the $H_2Pc/PV$ derivative (100 nm/100 nm) excited by 550-nm light (b). The dotted lines are the excitation light functions.

former decay could indicate lifetimes including the nano-second component. On the other hand, the previous results gave a much shorter lifetime component (5.5 ps) due to the high time resolution and narrow monitoring time region. The difference in the lifetimes was not attributed to experimental error, but to the experimental conditions, especially to the time region and time resolution.

We do not show the photoluminescence spectrum of the bilayer of $H_2Pc/PV$, because steady state photoluminescence spectrum was not observed when compared to the background intensity. The disappearance of the photoluminescence means a highly efficient quenching by the $H_2Pc$ layer. Such efficient quenching of the PV photoluminescence was reported for the multilayer with a 4-nm thick phthalocyanine and PV system.[10] The highly efficient quenching in the PV of the bilayer that was 25 times thicker than that of the reported system suggests the existence of a long range interaction as long as 100 nm in the PV layer.

The present photoluminescence decay of the PV in the bilayer was difficult to distinguish it from the scattering of the excitation light, and actually, the analysis gave no statistically satisfied single or double exponential function. To quantitatively discuss the decay of the bilayer, the relative photoluminescence yields of the bilayer ($\Phi_{bi}$) and monolayer ($\Phi_{mono}$) were compared. Because the data for monolayer and bilayer were obtained under the same experimental conditions including the counting time, the ratio of the total counted photon number should be the relative fluorescence yield,

$$\Phi_{bi} / \Phi_{mono} = \Sigma\, C_{bi}(n) \,/\, \Sigma\, C_{mono}(n) \qquad (3)$$

where $C_{bi}(n)$ and $C_{mono}(n)$ are the counted photon numbers at the time channel number "n" of the decays for the bilayer and monolayer, respectively. The calculated value of the ratio is negligible ($\Phi_{bi} / \Phi_{mono} = 0.075$), which is consistent with the disappearance of the steady state photoluminescence of the bilayer. The extremely low $\Phi_{bi} / \Phi_{mono}$ value indicates highly efficient quenching of the lifetime ($\tau_1 = 0.10$ ns), which is the major component ($\Phi_1 = 0.80$) of the decay.

Although the open circuit voltage of the photovoltaic $H_2Pc/PV$ (~0.55 V for 0.1 mW/cm$^2$ irradiataion)[4] is much lower than the applied field for the electric-field-induced quenching, the quenching of PV photoluminescence by the electric field (10% for 100 V/1.4 μm)[5] is less efficient than the quenching by $H_2Pc$, in spite of an excellent linear correlation with the carrier generation efficiency of PV. This fact shows that a different mechanism should be involved in the quenching by $H_2Pc$. The interface of $H_2Pc/PV$ should be responsible for the quenching. If a charge-transfer complex is formed at the interface, the efficiency of the charge separation, i.e., that of the $H_2Pc^+PV^-$ formation would be very high. Although the $PV^-$ generation at the interface could be one of the factors for the efficient quenching of the PV exciton, another interaction is required to explain the quantitative quenching of the exciton in the PV bulk. The reason should be due to the strong interaction between the exciton in the PV bulk and the $PV^-$ generated at the interface. In the previous report on the photovoltaic-effect of $H_2Pc/PV$, the open-circuit voltage and the fill-factor values were not significantly influenced by the thickness of the layer.[6] The insensitivity of the photovoltaic character to the thickness can be explained by the strong interaction between the exciton in the PV bulk and the photogenerated $PV^-$ with high mobility. Furthermore, the phototunable reflection property of $H_2Pc/PV$[13] agrees with the strong interaction to produce a high $PV^-$ carrier density. The n-type conduction in the PV layer would allow propagation of $PV^-$ photogenerated at the interface via electron carrier diffusion in the PV, which could explain the efficient quenching by $H_2Pc$, the photovoltaic effect, and the reflection tuning.

In conclusion, a remarkably efficient quenching of the photoluminescence of the PV by phthalocyanine was observed in both the steady state and time-resolved photoluminescence measurements. The quenched photoluminescent layer of the PV is so thick, that the interaction of the exciton in the bulk PV and the quencher ($PV^-$) generated at the interface of $H_2Pc$ would be very effective. The observed phenomenon is also informative to the n-type semiconducting character of the perylene derivative constructing an efficient photovoltaic cell and to the phototunable reflection by the perylene/phthalocyanine bilayer.

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