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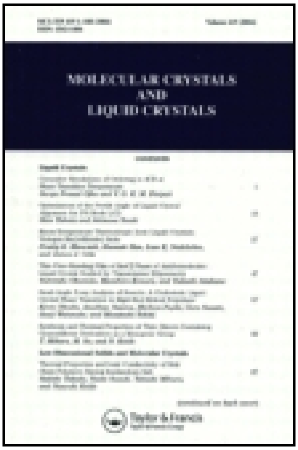

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Solid Phthalocyanine with High Fluorescence Efficiency

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Solid Phthalocyanine with High Fluorescence Efficiency

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A silicon phthalocyanine (Pc) compound $PcSi[OSi(CH_3)_3]_2$ in solid phase emitted a relatively intense fluorescence as compared with other solid Pc compounds. At room temperature fluorescence spectrum of the solid SiPc had three major bands peaking at 715, 781 and 840 nm, and total fluorescence yield was estimated to be $\sim 10^{-2}$, which was about 1/20 of that of solution. Different time-resolved decay profiles of these bands proved that the fluorescence had at least two emission origins. With decreasing temperature fluorescence intensity and spectrum changed drastically. In particular, below 60 K the 715 nm band became quite sharp and intense. Total intensity at 5 K was about ten times as large as that at 300 K.

Keywords: silicon phthalocyanine; fluorescence

INTRODUCTION

A recent report on electroluminescence emitted from a solid layer of metal-free phthalocyanine (H_2Pc)[1] prompts us to develop a new application of phthalocyanine (Pc) compounds as luminescent materials. However, fluorescence yields of solid (or condensed) Pc's are usually extremely small (for example, $\sim 10^{-4}$ for H_2Pc crystals[2]) even if molecular fluorescence yields are large (0.7 for H_2Pc monomer[3]). For practical purpose highly fluorescent solid materials are desired.

In searching for fluorescent solid Pc's, next two conditions would be indispensable. (1) Molecular fluorescence quantum yields are fairly large. (2) In solid phase, radiative decay rates of excited states are as comparably large as nonradiative decay rates. (Usual weak fluorescence of solid Pc's means that the latter are by far larger than the former.) As for (1), Pc compounds with light and diamagnetic center atoms would be favorable, avoiding the reduction of molecular fluorescence by heavy atom effect.[3] As for (2), though clear guiding principles have not been established yet, we guess that molecular packing is important. If neighboring molecules are arranged like face-to-face, transition from the lowest-lying singlet exciton state to the ground state is optically forbidden[4] and thus the exciton would be unable to convert to a photon. Hence, it seems at first necessary to avoid face-to-face arrangements. For this propose, Pc compounds with out-of-plane ligand(s) coordinated to the center metal atom seems favorable since stereochemical obstruction is expected.

Along these lines, we directed our attention to five- or six-coordinated Pc's with light center atoms and out-of-plane ligand(s) (AlClPc, TiOPc, $SiCl_2Pc$, $SnCl_2Pc$, $PcSi[OSi(CH_3)_3]_2$, etc.), and measured their fluorescences in solid phase. As a result, we found that $PcSi[OSi(CH_3)_3]_2$ emits relatively intense fluorescence. The fluorescence was by far intense compared with solid H_2Pc. In the following we report basic properties of the fluorescence of this material and shortly discuss its emission mechanism.

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EXPERIMENTALS

$PcSi[OSi(CH_3)_3]_2$, having been purified by sublimation, was provided by Toyo Ink Mfg. Co., Ltd. A thin film of this material was prepared on a quartz substrate by vacuum deposition. As a reference, chloroform solution of $PcSi[OSi(CH_3)_3]_2$ (1.8×10^{-5} mol/l) was prepared and sealed in a 1-mm thick glass cell. Absorption spectra of the film and the solution was measured by a conventional spectrophotometer Hitachi U3400. Using a He-Ne laser (632.8 nm) for excitation, fluorescence spectra were measured by an optical multichannel analyzer (OMA) Hamamatsu PMA-11 (C5966 model), spectral response of which had been calibrated,. To compare relative fluorescence efficiency of the film with that of the solution, backward configuration, shown schematically in Figure 1, was adopted. Scattered laser light was eliminated with a filter. Fluorescence spectra of the film at low temperatures were also measured using a cryostat. In this case fluorescence was detected from a direction perpendicular to the excitation light. Fluorescence decay was measured with a time-resolved fluorescence spectroscopy system consisting of a Hamamatsu Model C4334 streak camera connected to a polychromator Hamamatsu C5094, etc. A picosecond semiconductor laser Hamamatsu PLP-02 (660 nm, 60 ps pulse width) was used as an excitation source.

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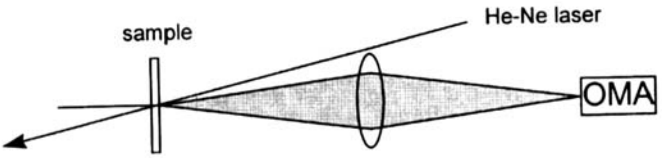

FIGURE 1 Backward Fluorescence Measurement Configuration.

RESULTS AND DISCUSSION

Fluorescence Spectrum and Efficiency at Room Temperature

Figure 2 illustrates absorption (ABS.) and fluorescence (FL.) spectra of the solution and the solid film. Q-band absorption spectrum of the solution, having a strong (0-0) band and weak vibronic bands, is typical of Pc molecules. Fluorescence spectrum of the solution shows a mirror image of the absorption spectrum with very small Stokes shift (probably the (0-0) band is somewhat weakened by reabsorption). Absorption spectrum of the solid film is broader than that of the solution, but as a whole it seems to retain the spectral character of the molecule. Fluorescence spectrum of the film in < 800 nm region resembles the solution spectrum apparently but additional bands appear in > 800 nm region. Stokes shift is also very small.

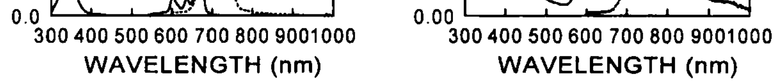

FIGURE 2 Absorption and Fluorescence Spectra of a Solution and a Thin Film of $PcSi[OSi(CH_3)_3]_2$.

Relative emission efficiency of the solid film was estimated to be about 1/20 of that of solution by comparing the values of (spectrum area / amount of absorbed photons). Although fluorescence quantum yields of SiPc molecules have not been reported, we infer that they are ~ 0.5 from an extrapolation using the values of Pc's whose center atoms locate in the same periodic row (0.6 for MgPc [3] and 0.58 for AlClPc[5]). Accordingly, we estimate quantum yield of the solid film to be ~ 10^{-2}. This value is two orders larger than those of H_2Pc crystals.

Time-Resolved Fluorescence Measurements at Room Temperature

To see emission dynamics in the solid, fluorescence decay of the distinct three bands peaking at 715, 781 and 840 nm was measured. As shown in Figure 4 these bands decayed differently. By deconvolution with the laser profile, the initial decaying profile of the 715 nm band could be analyzed single-exponentially with a 0.11 ns decay component, but to fit the full profile containing the tail region a double-exponential decay (0.08 ns and 0.26 ns) was necessary. The decaying profile of the 840 nm band could be analyzed by a 0.48 ns single-exponential decay. However, it was impossible to deconvolute the rising profile with the laser profile assuming simultaneous start of the 0.48 ns decay. This suggests a possibility of delayed fluorescence of the 840 nm band. The decaying profile of the 781 nm band could be analyzed double-exponentially with 0.11 ns and 0.48 ns decay components.

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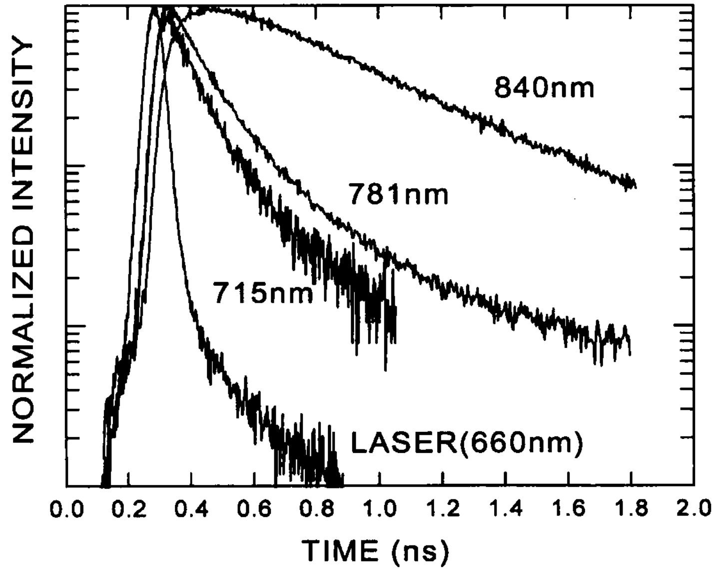

FIGURE 3 Fluorescence Decay Profiles of the $PcSi[OSi(CH_3)_3]_2$ Film.

From these results it is evident that the fluorescence has at least two emission origins. This is quite different from the case of the solution where all bands showed the same (5.6 ns) single-exponential decay. Probably the emission species of the 840 nm band are created not by the laser excitation but by relaxation from other spieces.

Fluorescence Spectra at Low Temperatures

Fluorescence spectra of the solid film were measured at various temperatures from 300 K to 5 K. As temperature decreased, the fluorescence spectra changed drastically as shown in Figure 4.

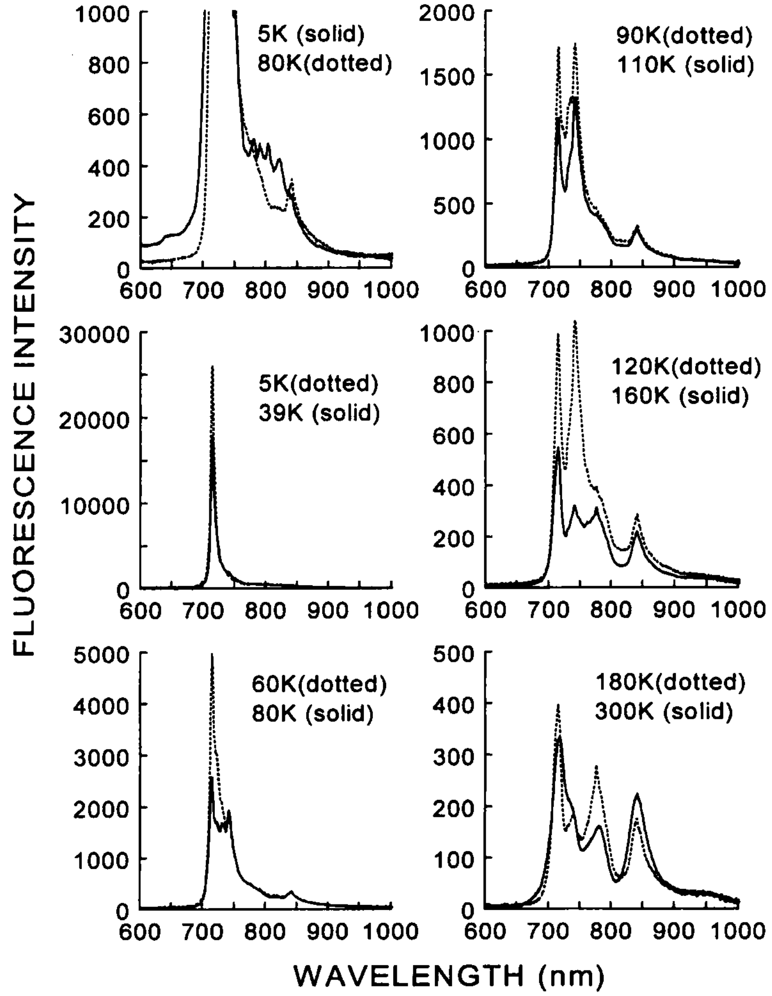

FIGURE 4 Fluorescence Spectra of the PcSi[OSi(CH_3)$_3$]$_2$ Film at Low Temperatures. Intensities are normalized.

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Temperature decrease from 300 K to 180 K induced an intensity decrease of the 840 nm band, an intensity increase of the 780 nm band, and a separation of the 742 nm band from the 715 nm band. Further temperature decrease to 110 K induced a rapid growth of the 742 nm band and a distinct appearance of the broad band in the valley between the 780 nm band and the 840 nm band. The 742 nm band had a maximum intensity at 80 K and reduced its intensity with further temperature decrease. At temperatures below 60 K, the 715 band became quite sharp and intense. Total intensity at 5 K was about ten times as large as that at 300 K. This intensity is comparable to monomer intensity but the lack of vibronic bands indicates that the fluorescence does not come from monomers. The development of the highest energy band at liq. He temperature has been also reported for H_2Pc crystal[6] but present band is much sharper.

The absorption spectrum of the solid film fairly retains the spectral character of the molecule as compared with ordinary Pc crystals with large spectral shifts. This indicates that intermolecular interaction between chromophores (Pc rings) is not so strong. This may be because intermolecular distances are enlarged by massive $OSi(CH_3)_3$ parts attached to central silicon atom from out-of-plane sides[7]. At this stage we are not sure of the reason for the relatively intense fluorescence of the material. The very intense fluorescence at low temperatures is considerably quenched below liq. N_2 temperature. This suggests that nonradiative quenching processes are largely activated in the temperature region.

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