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GAS DETECTION BY A MULTI-HYBRID SENSOR WITH DYE LANGMUIR-BLODGETT FILMS DEPOSITED ON A QUARTZ OSCILLATOR

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Abstract A hybrid gas sensor combined an optical detector with a weighing system for adsorbed gas is realized by dye LB-films deposited on a quartz oscillator. With this sensor, the change of fluorescence intensity from dye LB-film is simultaneously measured with the change of oscillation frequency of the quartz oscillator which depends on the amount of adsorbed gas in the LB-film. Squarylium dye LB-film and perylene dye LB-film were applied for this hybrid gas sensor. The quartz oscillators with LB-film commonly showed decrement of their oscillation frequency corresponding to the adsorption of gases. On the other hands, changes of fluorescence intensity depend on the type of gases, the dye molecules and its aggregation forms. These results suggest advantage of a multi-hybrid gas sensor using multiple quartz oscillators with different dye molecules. In this report, we discuss the responses of hybrid gas sensor in connection with the semiconductivity of the dye and its aggregate in LB-films.

INTRODUCTION

In recent years, there have been increasing interests in making of functional devices with organic molecules in organized structures. Gas detectors with organic thin films made by Langmuir-Blodgett technique is one of the most possible applications, because the thinness and the highly ordered structure of LB-film can be expected to improve the reversibility and response times[1~3].

We have studied an optical gas sensor using reversible quenching of fluorescence from J-aggregates of squarylium dye LB-film by ppb level of NO_2 in air[4]. High efficiency of fluorescence quenching and fast responses suggested a high performance of this system. To discuss the process of the NO_2 adsorption with the change of fluorescence intensity by adsorbed gas molecule, we proposed a hybrid gas sensor made by deposition of the dye LB-films on a quartz oscillator[5]. With this hybrid gas sensor, fluorescence intensity from the dye LB-film can be measured with the mass of adsorbed gas molecules simultaneously. On the responses for NO_2 gas, density of

adsorbed gas molecules was calculated by the change of oscillation frequency with the ratio of fluorescence quenching. Calculated number of squarylium dye molecules quenched by one NO_2 adsorbed molecule was about 50 under a condition when density of adsorbed NO_2 molecules was much less than that of squarylium dye molecules. This result suggests the effective area of fluorescence quenching for one trapping site made by adsorption of one NO_2 molecule to a squarylium dye molecule. Furthermore, fluorescence enhancement was observed on adsorption of NH_3 gas and there were decrement of oscillation frequency on exposure to vapor of trichloroethylene without any change of the fluorescence intensity. These responses of the hybrid gas sensor for other gases shows the possibility to recognize type and concentration of gases by integration of informations from the two different measuring systems on one detector. There were two important points in these results. One is the high mobility of excited states in J-aggregate seems to amplify the ratio of fluorescence quenching which results in high sensitivity for NO_2. To clarify the merit of using dye J-aggregate for optical gas detection, we must compare the ratio of fluorescence quenching of LB-film containing J-aggregate and other aggregate to the density of adsorbed NO_2 molecules. Another point is that the change of fluorescence intensity is caused by the electrical interaction between dye and gas molecules which must be depend on the semiconductivity of dye molecule. Hybrid gas sensor with other dye LB-films is expected to show different pattern of responses for gases from that of squarylium dye which will suggest the possibility of effective multiplection of the hybrid gas sensor.

In this report, responses of the hybrid gas sensor of squarylium dye LB-film containing its aggregate close to monomeric species is discussed with the comparison of the sensor containing J-aggregate. We also discuss for a hybrid gas sensor of another dye molecule. Squarylium dye shows p-type semiconductivity in xerographic studies which means the major carrier is hole in its conductivity. We assumed that the response of optical gas detection using the change of fluorescence intensity from squarylium dye must depend on its p-type semiconductivity. In this study, we prepared a hybrid gas sensor of n-type semiconductive perylene dye LB-film and discussed on the responses for gas detections in relation with the type of semiconductivity.

EXPERIMENTAL DETAILS

A piezoelectric crystal (10 MHz At-cut quartz with polished surface on which Au electrode had been deposited) (Showa Crystal) was used as a substrate of LB-film. The calculated density of adsorbed mass on both the sides of this quartz oscillator corresponding to decrement of the oscillation frequency for 1Hz is 2.21×10^{-9} g/cm^2. Chemical formula of two types of squarylium dye (SQ33 and SQ36) and a perylene dye derivative (PE) used in this work are shown in fig.1. LB-films of these dye molecules were deposited on the quartz oscillators from their mixed monolayers with arachidic acid (AA) and stearylamine (SA). For the deposition of squarylium dye LB-films, monolayers of SQ33 and SQ36 mixed with AA with same molar ratio were prepared on a pure water under surface pressure of 30 mN/m and at subphase temperature of 20°C. For perylene dye, a monolayer of PE and SA mixed with molar ratio of 1:5 was prepared on a subphase of pure water containing 3.0×10^{-5} M of $KHCO_3$ at 20 °C under surface pressure of 15mN/m. Quartz oscillators covered with three monolayers by Y-type deposition on both sides were used for gas detection. By measured decrements of the oscillation frequency for the deposition of each monolayers, calculated densities of dye molecules on the quartz oscillators were 1.29×10^{15} molecules /cm^2 for SQ33, 1.06×10^{15} molecules /cm^2 for SQ36 and 2.19×10^{14} molecules /cm^2 for PE.

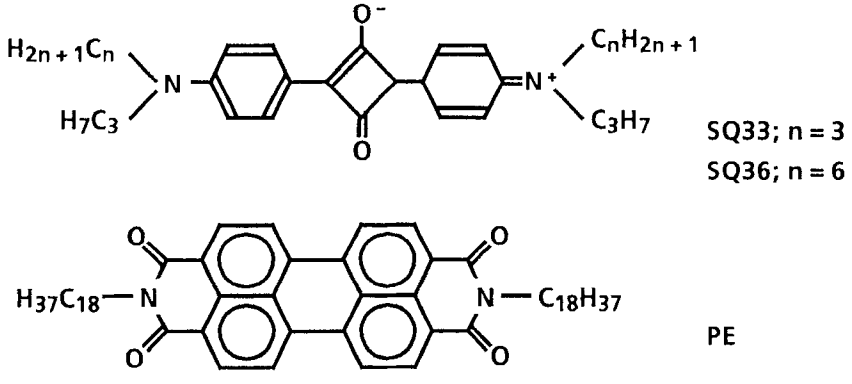


FIGURE 1 Chemical formula of dye materials

A quartz oscillator deposited with the dye LB-film was installed in a teflon reactor with a quartz window. For excitation of the dye LB-films, a 2

mW He-Ne laser was used for squarylium dye and a 3 mW Ar laser for perylene dye. The fluorescence intensity of each peak wavelength was monitored by a MCPD-100 (Otsuka Denshi) spectrophotometer through the window. The gas detector was connected to an oscillation circuit (USI System), and its oscillation frequency was monitored by universal counter HP-5334B (Hewlett Packard). The reaction gases were prepared by diluting the gases from a gas permeater PD-1B (Gastec) with pure air (grade S, Nihon Sanso) under flow rate of 2 l/min. Even at the time before and after the introduction of gas, the flow rate was kept constant with the pure air.

RESULTS AND DISCUSSION

Squarylium Dye LB-Film

Squarylium dye LB-films of SQ33 and SQ36 mixed with arachidic acid contains different aggregate[6]. Fig. 2 and 3 show absorption and fluorescence spectra of the LB-films. LB-film of SQ33 exhibits a sharp absorption band at

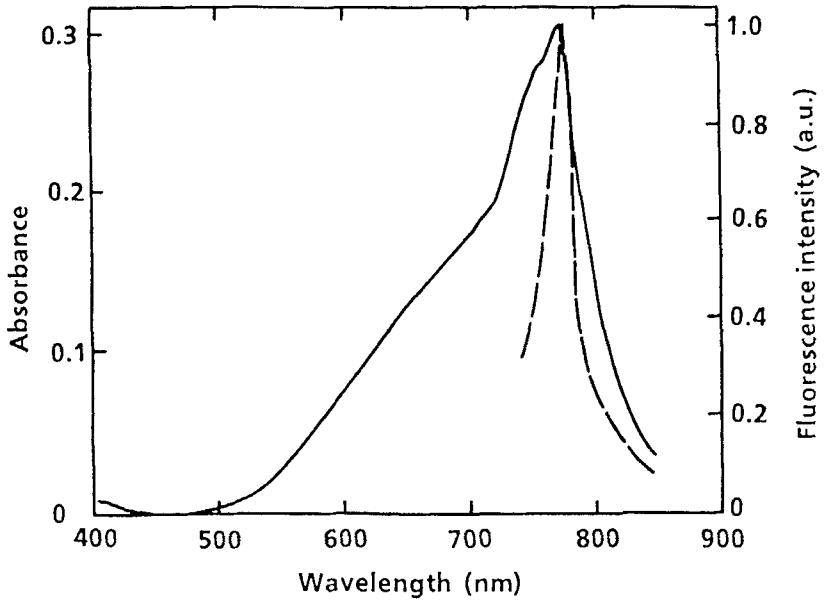


FIGURE 2 Absorption (—) and fluorescence (- -) spectra of SQ33 LB-film mixed with AA (3 layers).

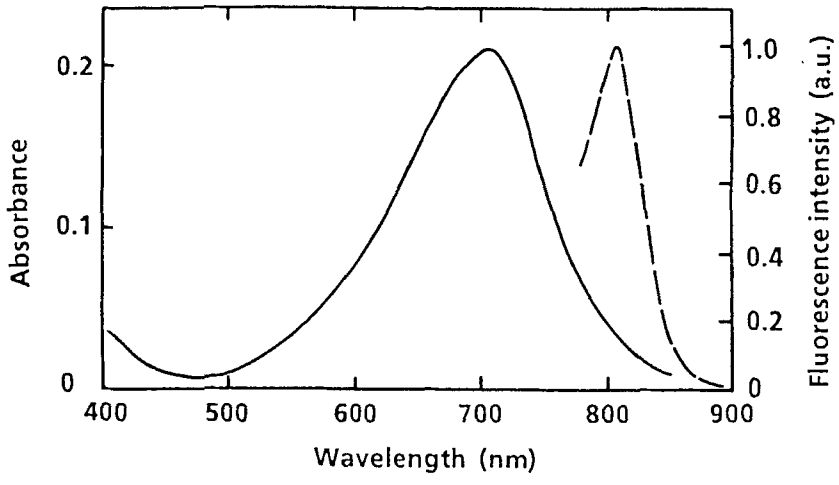
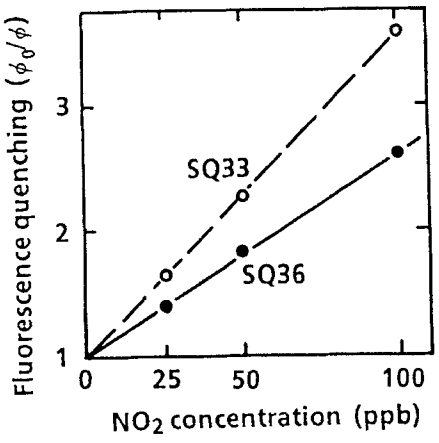


FIGURE 3 Absorption (—) and fluorescence (- -) spectra of SQ36 LB-film mixed with AA (3 layers).

about 770 nm with shift of a long wavelength to red from its monomeric band of solution (638nm). There are also sharp fluorescence peak with small Stork's shift which is characteristic of J-aggregate. On the other hand, absorption spectra of SQ36 LB-film exhibits a much broad band with a peak wavelength of 700 nm, which is less red shifted than that of SQ33 J-band. Fluorescence peak wavelength of this LB-film is 807 nm and the Stork's shift from absorption peak is also much larger than J-aggregate of SQ33. For the hybrid gas sensor using SQ36 LB-film, fluorescence quenching by adsorption of NO_2 is also observed. Fig. 4 shows Stern-Volmer plot of the fluorescence quenching on the concentration of NO_2 in air. By Stern-Volmer equation

$$\frac{\phi_0}{\phi} = 1 + k_q \tau_0 [Q] \qquad (1)$$

where ϕ_0 is the fluorescence efficiency in absence of quencher, ϕ in presence of quencher, k the rate constant for quenching of excited states, τ_0 the life time in absence of a quencher, [Q] the quencher concentration. In this case quencher is NO_2. Almost linear relationship crossing 1 on Y axis for both plots suggests only one kind of excited states are quenched with a same process on each LB-film. Quenched ratio of fluorescence from SQ36 LB-film on the concentration of NO_2 is a little smaller than that of SQ33. For the amount of adsorbed NO_2 molecules on the change of oscillation frequency,



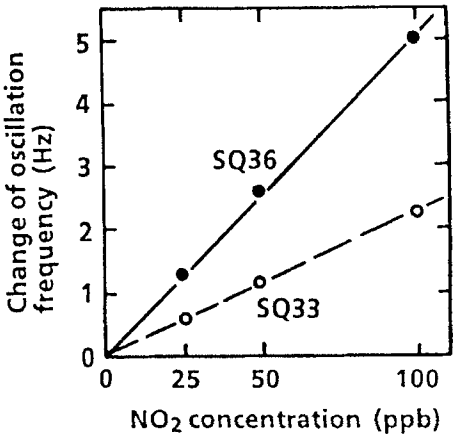


FIGURE 4 Stern-Volmer plot of fluorescence quenching by concentration of NO_2 in air.

FIGURE 5 Change of oscillation frequency on the concentration of NO_2 in air.

LB-film of SQ36 exhibits more than twice larger value than SQ33 as shown in fig. 5. Density of dye molecules in LB-films can be calculated from the change of oscillation frequency by the deposition of monolayers. Density of adsorbed gas molecules to the LB-films also can be calculated from the change of oscillation frequency by exposure to the gas. Fig. 6 is the Stern-Volmer plot of fluorescence quenching on the ratio of squarylium dye and NO_2 molecules calculated by each density. Fluorescence quenching ratio of SQ36 is much less than that of SQ33 for the adsorbed NO_2 molecules. From the following rearrangement of the Stern-Volmer equation,

$$\frac{\Delta S}{[Q]} = \frac{k_q \tau_0 S_0}{1 + k_q \tau_0 [Q]} \tag{2}$$

where ΔS is the density of quenched dye molecule and S_0 the density of all dye molecules, we can calculate the number of quenched dye molecules by one trapping site of fluorescence quenching made by the adsorption of one NO_2 molecule. In the condition where fluorescence quenching is very small ($kq\tau_0[Q] \ll 1$), the number of molecules is obtained shown below,

$$\frac{\Delta S}{[Q]} = k_q \tau_0 S_0 \tag{3}$$

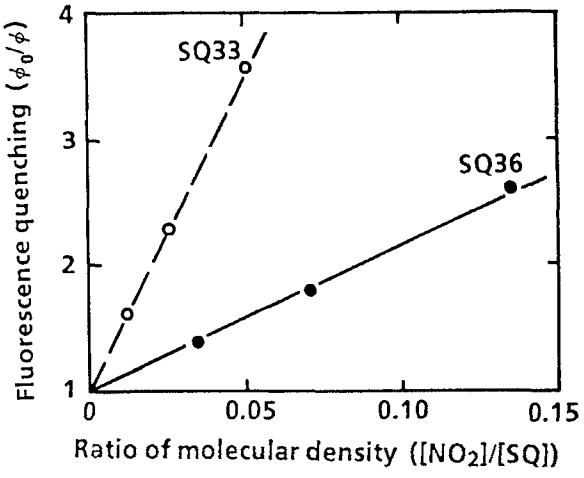


FIGURE 6 Stern-Volmer plot of fluorescence quenching by ratio of adsorbed NO_2 molecules for squarylium dye molecules.

where $k_q\tau_0$ is introduced by the slope of the Stern-Volmer plot and S_0 is calculated from the change of oscillation frequency by the deposition of the LB-film. For the LB-film of SQ33 containing it's J-aggregate, the calculated number was about 50 [5]. In this time, the number of 11.5 is observed for the LB-film of SQ36. These calculated numbers suggest that the number of squarylium dye molecules quenched by one trapping site for the aggregate in SQ36 LB-film is smaller than that of SQ33 J-aggregate. This result must reflect the magnitude of region where excited energy can migrate in it's lifetime around the domain of each dye aggregate which depend on the aggregation form and it's size. From extended dipole model proposed by H.Kuhn et. al., value of red shifted wavelength of absorption band of the aggregate from its monomeric band depends on the arrangement angle of molecules in the aggregate and the number of dye molecules constructing the aggregate[7]. Larger amount of adsorbed NO_2 molecules for LB-film of SQ36 under same concentration of NO_2 in air also suggests more adsorption sites reflecting smaller size of the aggregation structure.

Perylene Dye LB-Film

Absorption and fluorescence spectra of PE LB-film mixed with SA is

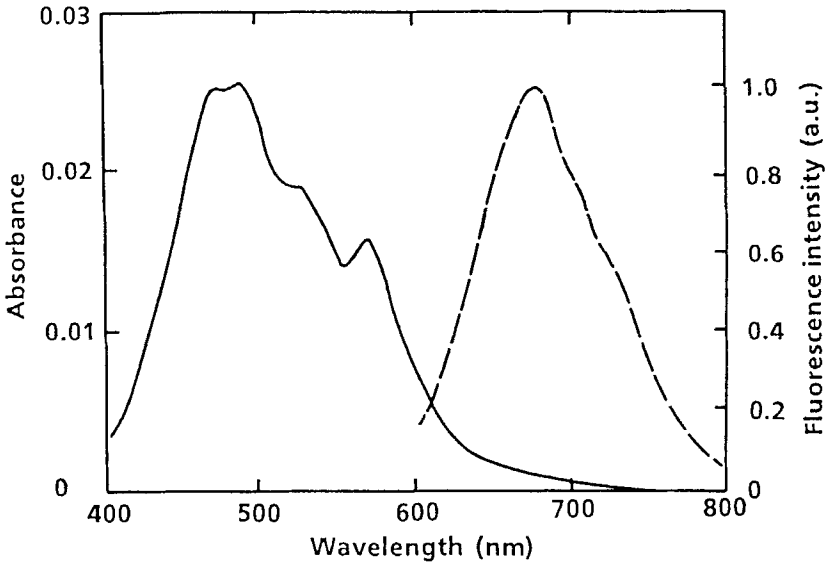


FIGURE 7 Absorption (—) and fluorescence (- -) spectra of PE LB-film mixed with SA (3 layers).

shown in fig. 7. Absorption peak of it's solution in chloroform is at 526 nm and fluorescence spectrum shows clear mirror image with a peak wavelength of 532 nm. Difference in these spectrum suggests the existence of some aggregation forms in the solid LB-film. Fluorescence intensity of peak wavelength (670 nm) is used for optical gas detection. Response curves of the hybrid gas sensor with perylene dye LB-film are shown in fig. 8~10. For the vapor of organic solvent (trichloroethylene), decrement of oscillation frequency by the adsorption of gas molecules is observed without any change of fluorescence which is a same result as the case of squarylium dye. On the other hand, fluorescence enhancement for NO_2 and quenching for NH_3 are observed in this time. Slow recovery of oscillation frequency was observed for NO_2 gas as shown in fig. 8. Such a slow recovery must be caused by high affinity of SA to NO_2 gas, because recovery of fluorescence intensity is much faster and response on the change of oscillation frequency of a hybrid gas sensor of PE LB-film mixed with AA was much smaller. The direction of fluorescence intensity change are opposite to the squarylium dye. The response of optical gas detection depends on the characteristics of dye molecule and these results must be reflected by the type of semiconductivity,

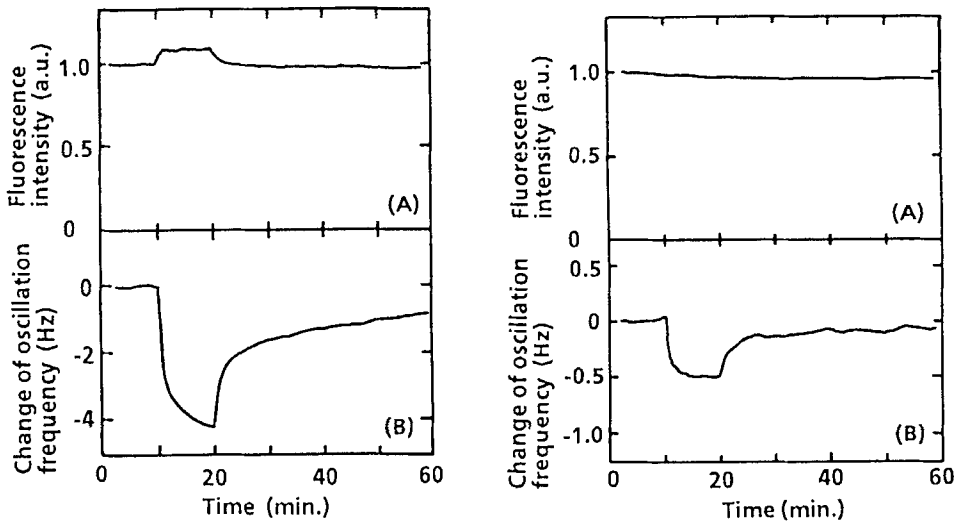


FIGURE 8 Change of fluorescence intensity (A) and oscillation frequency (B) on exposure to NO_2 gas (25 ppb) from 10 to 20 min.

FIGURE 9 Change of fluorescence intensity (A) and oscillation frequency (B) on exposure to vapor of trichloroethylene (200 ppm) from 10 to 20 min.

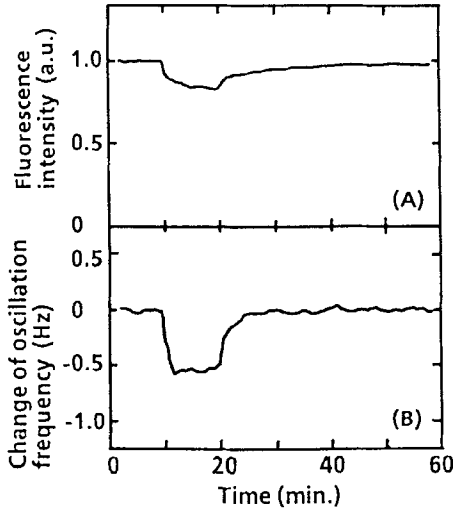


FIGURE 10 Change of fluorescence intensity (A) and oscillation frequency (B) on exposure to NH_3 gas (25 ppm) from 10 to 20 min.

where squarylium dye is to be a p-type semiconductive and perylene dye to be an n-type.

In the case of NO_2 gas detection by squarylium dye LB-film mixed with AA, it was not difficult to maintain values of adsorbed ratio of NO_2 molecules to the squarylium dye molecules because the squarylium dye adsorbs much more NO_2 molecules than the matrix of AA and the substrate of quartz oscillator. To determine the value of adsorbed NH_3 molecules to perylene dye molecules with ratio of fluorescence quenching, we chose SA for the matrix of PE which adsorbs much less NH_3 molecules than AA. Although using SA for the matrix of PE, affinity of PE for NH_3 gas is not so high and observed changes of oscillation frequency by NH_3 adsorption showed similar values for LB-films with different mixing ratios of PE and SA. Fig. 11 is the Stern-Volmer plot on fluorescence quenching of PE on the density of adsorbed NH_3 molecules in the LB-film on exposure to the NH_3

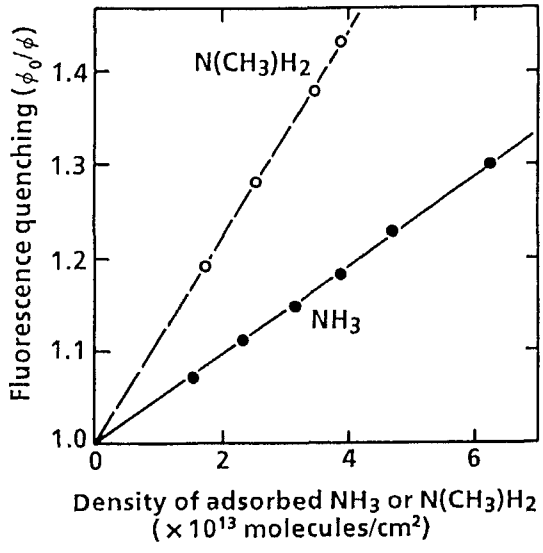


FIGURE 11 Stern-Volmer plot of fluorescence quenching by density of adsorbed NH_3 and $N(CH_3)H_2$ molecules in the LB-film.

concentration from 2.5 to 32 ppm in air. Linear relationship of fluorescence quenching on the density of NH_3 molecules suggests the interaction between perylene dye molecules and NH_3 molecules linearly increases with the enhancement of the density of adsorbed NH_3 molecules. If the adsorbed NH_3

molecules are dispersed uniformly in the LB-film, calculated number of quenched PE molecules by the one trapping site made by adsorption of one NH_3 molecule is about 3. The number of quenched dye molecules by one quencher molecule depends on the magnitude of the region where one trapping site affect to vanish the excited states of the dye which must depend on the mobility of excited energy in the dye aggregate and also on the effective distance of interaction between dye and adsorbed gas molecules. Enhanced fluorescence quenching for the adsorption of gas molecules is observed for $N(CH_3)H_2$ gas with concentration between 2.7 and 11 ppm in air as shown in Fig. 11. This result suggests longer distance of affection by an adsorbed $N(CH_3)H_2$ molecule than an NH_3 molecule for fluorescence quenching of PE LB-film which seems to depend on basicity of each gas.

CONCLUSIONS

Deposition of the dye LB-films on the quartz oscillator provides the hybrid gas detection method of fluorescence intensity measurement together with weighing the mass of adsorbed gas. From this hybrid gas detection, the ratio of the number of dye molecules quenched by one NO_2 molecule adsorbed on the SQ36 LB-film is observed for 11.5 which is smaller than the value of 50 observed for J-aggregate in SQ33 LB-film. This result suggests the amplification of optical responses by the migration of excited stats in aggregate depends on its form and the size. It will be necessary to observe views of molecular resolution by such as a scanning tunneling microscope or an atomic force microscope for these dye aggregates to discuss in more details.

Optical responses of perylene dye LB-film hybrid gas sensor shows in opposite directions for NO_2 and NH_3 to that of squarylium dye. Type of semiconductivity of the dye reflects on the optical responses of fluorescence quenching or enhancement which suggests that electrophilic attack of adsorbed gas molecules such as NO_2 made trapping sites of excited states on p-type semiconductive dye and nucleophilic attack of adsorbed gas molecules such as NH_3 quench fluorescence of n-type semiconductive dye. Observed enhancement of quenching ratio for $N(CH_3)H_2$ indicates difference of effective quenching distances in the variety of basic gases and suggests the possibility in discrimination of the kind of gases by the ratio of fluorescence

quenching on the density of adsorbed gas using the responses of two measuring systems. We have examined the hybrid gas detection method on squarylium dye and perylene dye and observed different pattern of responses in optical and weighing gas detection. If we use more variety of dye LB-films, each hybrid gas sensor is expected to response in its own manner. Multiple hybrid sensor have possibility to be improved into a more intelligent system which recognize complicated gas type and concentration in complex conditions with high sensitivity, simply and effectively.

In the olfactory organ, there are number of sensory neurons with different balance of constituents in their membrane. Different pattern of impulses is generated by the depolarization of each cell for an odorant. By the information processing of these impulses in the neural system, sensations and recognitions of smells are formed[8]. There have been some works on the model of olfactory receptor using weighing system of adsorbed gas with lipids films coated on a quartz oscillator[9] and multiple sensors connect with an artificial neural network system[10].

We believe new type of sensor which has ability of recognition of gases with high performance comparable to the biological system will be developed not only providing multiple detectors but also using hybrid detection method because of its clear selectivity and amplification by dye aggregate. It is also expected to develop a information processing system such as learning devices by also organic materials which will be connected with the receptors directly.

We want to maintain that this hybrid gas detection method is also effective in the study of quantitative characterization for organic semiconductors in connection with its fluorescence properties. For a more accurate analysis, inhibition of nonspecific adsorption of gases for substrate containing matrix molecules by selection of materials or some treatment must be needed.

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