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Photoinduced Oxidation Reaction of Evaporated Rubrene Thin Films Studied by Spectroscopic Measurements

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Abstract

In the field of organic electronic device research, elucidating the microscopic mechanism of the oxygen effect is important because degradation of the electronic properties by ambient oxygen is a major concern. This study focuses on rubrene, which exhibits excellent hole conductivity in its crystalline form. Rubrene is oxidized under an ambient environment, but the oxidation mechanism of thin films is unknown. Specifically, we investigate the photoinduced bleaching kinetics of vacuum-evaporated rubrene thin films by electronic spectroscopy and the structure of the photoinduced product by infrared vibrational spectroscopy. The photoreaction rate depends on film thickness. In addition, we confirm that the photoreaction product is rubrene peroxide using theoretical calculations.

Key words: Organic semiconductor, Photo-oxidation, Vibrational spectroscopy, Rubrene, Quantum chemical calculation

1. Introduction

Recently, electronic devices utilizing organic molecules have attracted much attention due to advantages such as low-cost and excellent productivity compared with their conventional inorganic counterparts. There has been a continuous demand for organic thin films that exhibit outstanding electronic conductivities. In particular, the rubrene single crystal has gathered considerable attention because it has the largest reported field effect carrier mobility of any organic material¹. However, a rubrene molecule in solution is chemically converted into rubrene endoperoxide in the presence of oxygen and UV light, and a similar oxidization has been suggested to degrade the hole conductivity in thin films²-⁴. Despite several studies on the photodegradation of rubrene solid films, the deterioration mechanism and chemical identification of the product have not been fully achieved. Therefore, a comprehensive investigation on the photoinduced oxidation of rubrene thin film is highly desirable.

In this study, we focus on the photoinduced reaction of rubrene thin film under ambient conditions. Although several works have studied the photobleaching kinetics, none have reported the dependence of the photobleaching kinetics on film thickness. In addition, previous works have yet to identify the chemical structure of the photoreaction product by vibrational spectroscopy. Herein we investigate the dependence of the photoinduced reaction kinetics on film thickness via UV-visible absorption spectroscopy as well as identify the structure of the reaction product after photoinduced oxidation using infrared vibrational spectroscopy combined with theoretical predictions.

2. Experimental Procedure

2-1 Fabrication of Rubrene Thin Films

Rubrene thin films were fabricated by vacuum vapor deposition in a high vacuum chamber (base pressure less than 1.29 × 10⁻⁴ Pa). Sublimated rubrene molecules were deposited on quartz or silicon substrates at a rate of 3.2 nm/min at room temperature. Figure 1 shows a picture of a sample. Quartz substrates were used for visible and ultraviolet spectroscopies, while silicone substrates were used for infrared spectroscopy. We fabricated three samples with different thicknesses (30, 100, and 200 nm), which were calibrated by a quartz microbalance.

2-2 Observation of the Photoinduced Oxidation Kinetics by Electronic Absorption Spectrum Measurements

We traced the photoinduced reaction processes by measuring the electronic absorption spectra as a function of irradiation time with actinic light. Samples were measured at room temperature in an ambient environment. The light source was a halogen lamp (2 mW) with a wavelength range of 400–800 nm, and continuum light was used for both actinic light of the photoreaction and the probe light for the absorption spectroscopy. The absorption measurement employed a transmission configuration, and the probe light was analyzed by a multichannel detector (HR2000, Ocean Optics). We examined the effect of film thickness on the photoreaction kinetics by measuring the kinetics for three different thicknesses (30, 100, and 200 nm).

2-3 Identification of the Photoproduct by Infrared Vibrational Spectroscopy

The infrared absorption spectra of the deposited films were measured by a Fourier transform infrared spectrometer (FTIR: IRRTracer-100, Shimadzu). The vibrational spectra of the rubrene films were measured before and after actinic light irradiation. We then identified the photoproduct along with the molecular structure by comparing the obtained IR spectra with the predicted result based on quantum chemical calculations, assuming the oxidized molecular structure via the expected
light-induced reaction. The density functional theory (DFT) calculations were implemented using the Gaussian09 software package with a B3LYP (6-31G) basis function\(^{(5)}\).

3. Results and Discussions

3-1 Light-induced Oxidization Process Dependence on Film Thickness

Figure 2 shows the visible-range absorption spectra for a 100-nm thick film. We have confirmed that the absorption spectra are independent of the film thickness (data not shown). The peaks observed at wavelengths of 458, 490, and 524 nm correspond to the \(S_0 \rightarrow S_1\) transitions and ascribed to the 0-0, 0-1, and 0-2 bands, respectively\(^{(6)}\). Figure 2 also shows the change of the absorption spectra as a function of the measurement times. Similar to a previous study\(^{(4)}\), the monotonic decrease in the absorbance of the absorption band implies that photobleaching occurs during light irradiation in air.

Figure 3 shows the decay curves of the absorbance as a function of the measurement time at wavelengths of 521–530 nm for the three thickness conditions, where the ordinate is normalized at the maximum absorbance for each thickness. We estimated the phenomenological reaction rates for the three kinetic curves by assuming a first-order reaction and fitting the obtained results with the least-square method. Table 1 lists the evaluated reaction rates.

The reaction rate depends on film thickness. The 200-nm thick film exhibits a reduced reaction rate, which is 0.2–0.3 times those of the 30-nm and 100-nm thick films. Three possible reasons are considered for this reduced reaction rate at a higher thickness. (1) The reactivity of rubrene is reduced as the film thickness increases. (2) The density of the rubrene excited state is reduced at a higher thickness due to the attenuation of the light intensity within the film. (3) The oxygen concentration inside the film decreases at the higher thickness due to the limited permeability of oxygen, reducing the likelihood of oxidizing rubrene.

First, (1) is unlikely because the molecular chemical reactivity is independent of film thickness. In addition, (2) is unlikely. From the absorption spectra in Fig. 2, the estimated maximum attenuation of the light intensity for the 200-nm thick sample is 0.63 times the incident light, but the reaction rate is as low as 0.2–0.3 times the incident light with the thinner films. The significant difference between the two indicates that the reduced reaction rate is not solely due to the reduced intensity of the light. Therefore, we consider that the remaining possibility (3) may contribute to the reduced reaction rate. The oxygen density in the inner part of the film decreases as the film thickness increases.

3-2 Infrared Vibrational Spectrum Measurements Before and After the Reaction

To investigate the change in the vibrational spectra due to photobleaching, we irradiated the rubrene films on silicone substrates with the halogen light for three hours. Then we measured the infrared vibrational spectra before and after the irradiation. The obtained results are shown in Fig. 4.

The change in the vibrational spectrum upon photoirradiation reveals three points. First, the peak at 586 cm\(^{-1}\) disappears and is replaced by two peaks at 571 and 621 cm\(^{-1}\). Second, the peak at 721 cm\(^{-1}\) is replaced by a more intense peak at 725 cm\(^{-1}\). Third, the relatively broad peak at 762 cm\(^{-1}\) is further broadened with a reduction in its intensity.
3-3 Prediction of the Vibrational Spectra based on Quantum Chemical Calculations

Figure 4 shows the predicted vibrational spectra from the DFT calculations for rubrene peroxide (Fig. 5) as well as for a rubrene molecule. The theoretical spectrum for the rubrene peroxide shares the same features as the experimentally observed one, especially for the three experimental signatures described above. Therefore, we conclude that the experimentally observed change in the vibrational spectrum is due to the production of rubrene peroxide via photoinduced oxidation of the rubrene molecules. Figure 5b shows an example of the vibrational displacement of a mode that significantly shifts upon oxidation (621 cm$^{-1}$).

4. Conclusion

This study investigates the reaction kinetics of deposited rubrene thin films with an emphasis on the visible photoinduced bleaching reaction by utilizing electronic and vibrational spectroscopies. The following points are revealed:

(1) Photobleaching of the rubrene thin film occurs when irradiating with visible light. The rate of change depends on the film thickness.

(2) The vibrational spectrum measurement combined with quantum chemical calculations on the targeted oxidized structure implies that the reaction product is rubrene peroxide.

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References

5. Gaussian09, Gaussian Inc., Wallingford, CT, 2009, revision a.1 ed.

ルブレン蒸着膜の光誘起酸化反応過程の分光計測

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要旨

近年,有機分子を用いた電子回路や素子の研究が活発に行われているが、有機分子は多くの場合、大気中の酸素により酸化され、電気的・光学的特性が変化するため、酸化反応機構を明らかにすることは重要である。ルブレンは単結晶状態での電気伝導性が優れていることで知られるが、特に可視光照射によって酸化反応が促進され、薄膜状態での酸化機構については不明な点が多い。本研究では、真空蒸着により作成したルブレン薄膜の光誘起酸化過程を可視吸収電子分光および赤外吸収振動分光を用いて調べた。大気下での可視光照射により、光酸化に起因する電子吸収帯の減少が観測され、膜厚に依存した反応速度の変化が観測された。また、光照射したルブレン薄膜について赤外吸収振動スペクトルを測定し、量子力学計算の結果と比較することで、光誘起酸化によりルブレンパーオキシドが生成していると結論された。

重要語句：有機半導体、光酸化反応、振動分光、ルブレン、量子化学計算

Fig. 5. (a) Structure of rubrene peroxide used in the vibrational mode analysis in Fig. 4. White, gray, and red spheres indicate hydrogen, carbon, and oxygen atoms, respectively. (b) Vibrational displacement of rubrene peroxide for the mode predicted at 621 cm$^{-1}$. 

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