Facile Synthesis of Coronene Dimers Having Unique Optical Properties

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Abstract: The authors synthesized very pure dimer phase of coronene by simple heat-treatment and subsequent sublimation purification. It was confirmed by laser desorption/ionization mass spectroscopy measurements that pure dimer phase of coronenes can be obtained by controlling the fusing and sublimation temperatures. The crystal structure of the dimer phase was analyzed by synchrotron XRD (X-ray diffraction) experiments. It was also found that very bright red light is emitted by irradiating ultra violet light ($\lambda = 350$ nm) to the dimer phase. The external and internal quantum yields were determined to be 5.56% and 6.95%, respectively.

Key words: Graphene, PAH, PL, LED.

1. Introduction

Since 2004, graphene has attracted much interest because of its unique physical and electronic properties [1, 2]. Furthermore, and in addition to its structural uniqueness, graphene has very fascinating physical and chemical properties. For example, graphene materials showed very good electrode properties for energy storage applications [3]. Among many research papers describing graphene’s fascinating properties, much progress in the research on the optical properties of GQDs (graphene quantum dots, namely the carbon cluster structure) has been achieved during the past decade [4, 5]. Carbon-based quantum dots including GQDs are superior in terms of high solubility, high chemical stability, facile modification, and so on. However, since it is usually not very easy to determine the exact structure of GQDs, theoretical approach on model structures tends to have quite a few ambiguities. Therefore, the synthesis of carbon clusters whose atomic arrangements are known is highly demanded. For this purpose, synthesizing graphene-like molecule by dehydrogenation reaction of PAHs (polycyclic aromatic hydrocarbons) would be a good approach. So far, the authors reported a facile synthesis method of graphene-like molecules from pentacenes, just by fusing them in a sealed glass tube [6, 7]. With this treatment, ribbon type graphene-like molecules consisting of several pentacenes can be formed. However, the obtained materials are mixture of graphene-like molecules having different sizes, and it is still difficult to obtain a specific size carbon cluster. Dehydrogenation reaction between two pentacenes occurs in a variety of manners, and size-controlled graphene synthesis starting from pentacenes is very hard (Fig. 1a). To control the structure of graphene sheet derived by fusing treatments of PAHs, the authors used a different kind of PAH: coronene. In this paper, the authors describe how to obtain structurally designed graphene sheet from PAHs.

The authors also discuss the optical properties of the size-controlled graphene-like molecules. Owing to the high energy efficiency of LED (light emitting diode), LED room lights are now rapidly spreading. However, since most of the commercially available LED room lights consist of blue LED and yellow fluorescence materials, emission spectra of LED room lights are quite different from that of solar light.
Instead of the present combination of blue LED and yellow fluorescence materials, new combinations of UV (ultra violet) LED and red-green-blue fluorescence materials are being explored. For the new combinations, the authors need to develop new fluorescence materials having high energy efficiency. For this purpose, some researchers are trying to control fluorescence color by changing π-conjugation scale of graphene. One of the purposes of the present study is to contribute to the above-mentioned LED research.

2. Experimental Sections

The authors purchased a reagent grade coronene powder sample (Tokyo Kasei Co. Ltd.). The powder sample of 30 mg was sealed in an evacuated silica glass tube and was heat-treated at several temperatures (400 °C, 500 °C, 600 °C and 700 °C) for 15 h. After the heat-treatment, the authors unsealed the glass tube to take the reacted sample out, and washed the sample using toluene and acetone repeatedly in order to remove unreacted coronenes completely. The washed samples were analyzed by mass spectroscopy measurements. Mass spectrum measurements were conducted using a LDI-TOF (laser desorption/ionization time-of-flight) mass spectrometer (JEOL JMS-S3000) equipped with a 349 nm wavelength UV laser as ionization source. The mass spectrometer was operated in positive-ion detection mode. The measurements were performed without using any matrix. The m/z scales of obtained spectra were externally calibrated with the decomposition peak positions of PEG (polyethylene glycol). The washed sample consisting of different cluster sizes were purified by sublimation at different temperatures. The sublimed samples were again analyzed by mass spectroscopy.

XRD (X-ray diffraction) measurements of the purified samples were performed on a synchrotron radiation beamline BL-18C at the Photon Factory in High-Energy Accelerator Research Organization (KEK), Tsukuba, Japan. The beam was monochromatized by Si (111) double monochromators and collimated by a pinhole collimator of 100 mm in diameter. The incident X-ray wavelength was set to \( \lambda = 0.0614 \) nm. The authors also observed photoluminescence spectra of the purified samples using JASCO FP8600 spectrometer at room temperature. The excitation source used in the present study was Xenon lamp monochromatic light (\( \lambda = 350 \) nm).

3. Results and Discussion

The way how two coronenes transform to a dimer is limited to the scheme shown in Fig. 1, while there are several possible structures of pentacene dimer as mentioned in the introduction section. The polymerization of coronenes would occur by extending the dimerization scheme shown in Fig. 1.

Fig. 2a shows the observed LDI-TOF mass spectrum of the polymerized coronenes prepared at 500 °C. It was found that polymerization up to at least tetramer occurred. However, it was also found that the material produced by a simple heat-treatment is the mixture of polymerized coronenes having different sizes. Therefore, as a next step, the authors tried to purify the polymer mixture. For this purpose, the authors performed a purification using the difference between the obtained polymers in terms of their sublimation temperatures as follows:

First, the authors put the polymer mixture in an evacuated glass tube. Then the authors heated the sample side of the tube with keeping the other side at low temperature. The authors changed the heating temperature in a temperature range of 400-600 °C and the sublimed samples were analyzed by mass spectroscopy. Fig. 2b shows the LDI-TOF mass spectrum of the sample that was polymerized at 500 °C and sublimed at 600 °C. As shown in Fig. 2b, only one peak is observed at 596 m/z, which corresponds to dimer phase of coronene (dicoronylene).

Although the mass spectrum of the sublimed sample (Fig. 2b) indicates that an almost pure dimer phase was prepared, the authors check the purity of
the sample by another method because the LDI-TOF mass detects only ionized fragment of the sample. Therefore, the authors performed synchrotron XRD measurement of the sublimed sample. Fig. 3 shows the observed and simulated XRD patterns. The simulation was performed using a previously reported crystal structure data of dicoronylene [8]. As shown in Fig. 3, the simulated pattern reproduces the observed pattern very well. So far, it was reported that dicoronylene crystals are synthesized by complicated multi-step organic reactions [9]. Although our method is very simple compared with the previous method, Fig. 3 shows that the method could produce a single phase of dicoronylene crystals very effectively.
Fig. 2  LDI-TOF mass spectra of the polymerized coronenes (a) before and (b) after purification.

Fig. 3  (a) Observed and (b) simulated XRD patterns of dicoronylene.
As mentioned in the introduction section, changing π-conjugation scale of graphene structures is one approach to obtain fluorescence materials with controlled fluorescence colors. Typically, a larger π-conjugation system has smaller band gap. Therefore, it should be possible to control the color of fluorescence light of graphenes by controlling their sizes. However, it is not easy for practical purposes to use solid graphene materials as fluorescence materials, because the energy gap of certain size graphene happens to fall within the infrared region, which causes quenching in solid phase to occur easily. Therefore, to control the polymerization of PAHs it is important to know the limiting size of graphene which can emit visible light. From such a point of view, the authors observed PL (photoluminescence) property of the obtained coronene dimers. As shown in Fig. 4, the fluorescence color of coronene is yellowish green. On the other hand, the PL peaks of dicoronylene were observed in higher wavenumber region than those of coronene monomer. It is well known that PL spectrum of coronene monomer changes depending on the environment of coronene [10]. However, such significant change in PL shape shown in Fig. 4 can not be explained by an environmental effect. It should be judged that PL shape also confirms the formation of dicoronylene.

To understand the PL mechanism, the authors observed excitation spectrum for emission of $\lambda = 650$ nm (Fig. 5). It was found that wide range light from low energy UV to visible region can be used as excitation light for $\lambda = 650$ nm emission. The authors evaluated the quantum yield for $\lambda = 350$ nm excitation light. External and internal quantum yields were determined to be 5.56% and 6.95 %, respectively. These experimental results show that coronene dimers prepared in the present study can emit very bright red light by UV-LED.
Facile Synthesis of Coronene Dimers Having Unique Optical Properties

4. Conclusions

Dicoronylene crystal was obtained from coronene monomers by a simple heat-treatment and a subsequent sublimation purification. The crystal structure was confirmed by synchrotron XRD experiments. It was also found that very bright red light is emitted by irradiating ultra violet light (λ = 350 nm) to the dimer phase. The external and internal quantum efficiencies were determined to be 5.56% and 6.95%, respectively.

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References


Fig. 5  Excitation light spectrum of the prepared dicoronylene.