Notes

Temperature Dependence of Calixarene Crystal Luminescence

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The study of calixarene has been of continuing research interest in the areas of host-guest chemistry,[1-4] inclusion compounds,[5-7] organic catalysts,[8,9] and analytical chemistry.[10,11] Calixarene is methylene linked phenolic macrocycles available in several cavity sizes, and a variety of functional groups at the top and bottom rims of cavity. Calixarenes could have four possible geometrical structures such as conc. partial conc, 1,2-alternate, and 1,3-alternate.[12,13] The remarkable chemical property of calixarene is its ability to dissolve a wide variety of other compounds, both in solution and in the solid state. Calixarene forms inclusion compounds by dissolving other molecules to form crystalline solids. These inclusion compounds can be formed with essentially any guest. The selectivity and orientation of guest molecules in the cavity depend on the size and functional group of guest molecules. The calixarene crystals have well defined structures and stoichiometries and sufficiently small disorder that even atoms of the guest molecules can be located by X-ray crystallography.[13] Calixarene may serve as a universal host for studies and utilization of optical phenomena in crystalline system, but essentially nothing is known about the optical properties of these material, although some characteristics have been reported.[14-16] Much of the photo-luminescence work on calixarene has been conducted on porous silicon coated with calixarene,[14] on water-soluble calixarene,[15] or on Langmuir-Blodgett films.[16] Here we report the investigation of the photoluminescence of calixarene crystals as functions of temperature, time, and exciton concentration. The particular derivatives of calixarene interested in this study contain butyl groups on their upper rim and hydroxyl groups on the lower rim with four phenol moieties.

Experimental Section

The calixarene crystals were prepared by slow cooling followed by slow evaporation of the solvent. After crystallization, the resulting crystals were rinsed with the solvent. The samples were mounted between quartz plates and in the closed cycled cryogenic system (APD CSW-202) to obtained the temperature between 12 K and 300 K. The excited states were generated by 325 nm radiation from a He-Cd laser (Liconix 3650N) for the steady-state spectra

measurements. The luminescence was monitored through a double spectrometer (Spex 1403) using a photomultiplier tube (Hamamatsu R943-02 GaAs) and current amplifier at a gain of 10^8 V/A. All the experiments were controlled by a computer. The spectra were collected using an analog to digital converter.

A pulsed Nd-YAG laser (spectra laser physics, SL825G) was used as excitation source for time-resolved spectra measurements. A photon counter was used for the time resolved data acquisition. The time response of the electronics was tested with a pulse generator.

Results and Discussion

A set of steady-state luminescence spectra of calixarene crystals for different temperatures obtained with 325 nm excitation is shown in Figure 1. The vibronic bands shift to longer wavelength and become significantly sharper as temperature decreases from 298 K to 12 K. For the case of spectrum at 298 K, steady-state fluorescence shows the three vibronic modes at 365 nm, 402 nm, and 500 nm. As temperature decreases to 12 K, the band at 365 nm significantly decreases in intensity and relatively sharp peaks appear at 402 nm and 430 nm, and the broad band at 500 nm
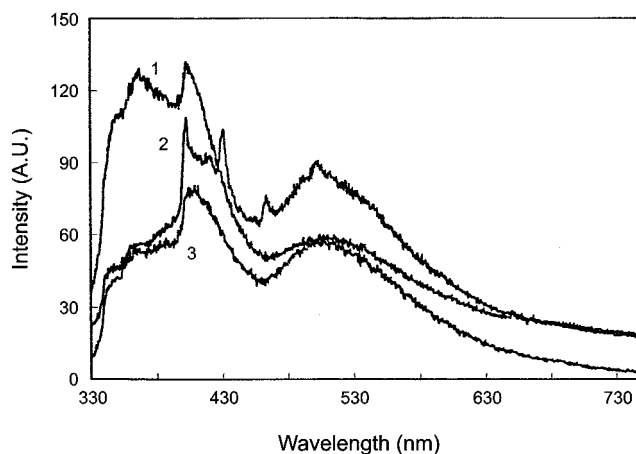

Figure 1. A set of steady-state luminescence spectra of calixarene crystals for different temperatures obtained with 325 nm excitation (1: at 298 K, 2: 12 K, 3: 298 K after annealing).

increases in intensity. The spectrum observed at 298 K, obtained after increasing temperature from 12 K (annealing), resembles that of the spectrum obtained at 12 K. but relatively broad due to thermally activated dispersions.

In order to understand the change of spectral features as temperature decreases. it is assumed that the spectrum at 298 K is connected with the luminescence of free excitons and the spectrum at low temperature is luminescence of excitons localized on structural defects. A luminescence spectrum was obtained with higher excitation energy. We expect the changes in the spectral position and bandwidth as density of states increases if the excitons fall into traps of the structural defects. However. no significant change in spectral features is observed. This results rule out the assumption because higher exciton population would increase the trapping efficiency to the structural defects and cause the spectra shift to longer wavelength. We now consider that there is a structural transformation from high temperature modification to low temperature modification as temperature decreases. Figure 1 also shows the spectrum at temperature of 298 K for the crystals after cooling down to 12 K. The band position of spectrum at 298 K after frequent cooling (annealing process) resembles the spectrum of 12 K. The experimental results demonstrate that the consideration of structural transformation seems to be quite reasonable. The changes of the spectral features may take place due to local temperature of sample by laser illumination. In order to determine this is not the case. the sample was cooled down to 12 K and heated to 298 K without laser illumination. The luminescence obtained for crystal annealed without laser illumination is identical with the one for the sample laser illuminated in the process of annealing. From the experimental results we conclude that structural transformation occur during the annealing process.

Time-resolved spectra of calixarene at 12 K for different delay times following excitation are shown in Figure 2. The excitation energy was 266 nm and the increment of delay time was 1 ns. The width and position of the band appear to be independent of the delay time. If there is an energy transfer from a high to low energy sites. we expect changes in spectral features. If energy transfer is controlled by
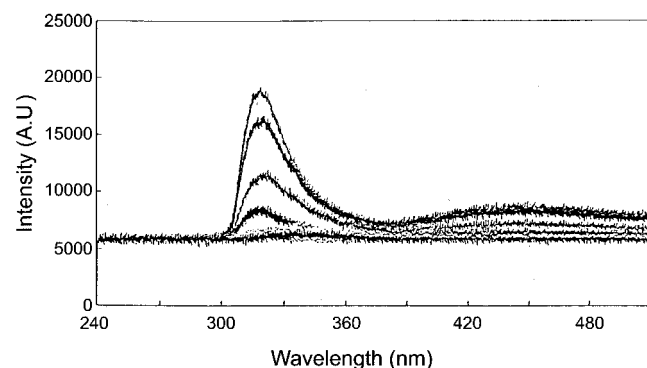
emission of phonons or vibrons. the excess energy must be dissipated by phonons or vibrons and a higher energy band will lose intensity and a lower energy band will gain intensity following the time of excitation. The experimental results imply that no site relaxation occurs after a site has been populated by an excitation. Low temperature luminescence spectra of matrix-isolated organic molecules usually exhibit a well-resolved zero phonon feature suggesting that spontaneous site relaxation after excitation is the exception rather than the rule.[17-19] If the density of states controls the rates. the band will gradually broaden and shift to lower energy sites. No cascade relaxation. however. is observed. The results indicate that the depopulation of excited state density is mainly controlled by monomolecular decay process dominating other decay processes. The linear semilog plot indicates that the time evolution of the fluorescence intensity of calixarene crystals is a simple exponential function of time. The lifetime of calixarene in the singlet excited state is found to be 2.6 ± 0.1 ns.

To summerize. experimental results of photoluminescence of calixarene crystals as a function of temperature reveal that a structural transformation from high temperature modification to low temperature modification occurred during the annealing process. The experimental results of time-resolved spectra of calixarene at 12 K demonstrate that the width and the position of the emission band appear to be independent of the delay time. The results indicate that the depopulation of the excited state density is mainly controlled by unimolecular decay process dominating other decay processes. The lifetime of calixarene in the singlet excited state is found to be 2.6 ± 0.1 ns.

Figure 2. Time-resolved luminescence spectra of calixarene at 12 K for different delay times with excitation at 266 nm (the increment of delay time is 1 ns).

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1156   *Bull. Korean Chem. Soc.* **2002**, Vol. 23, No. 8

Notes

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