# Energy Transfer between Calixarene and Naphthalene

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The photoluminescence of calixarene crystals has been studied as functions of temperature, time, and concentration. The vibronic bands shift to longer wavelength and become significantly sharper as temperature decreases. The experimental results reveal that the structural transformation occur during the annealing process. Time-resolved spectra of calixarene at 12 K are monitored. Spectral features, which demonstrate characteristic of energy transfer processes, are not observed. The depopulation of excited state density is mainly controlled by unimolecular decay process dominating other decay processes. The lifetime was found to be $2.6 \pm 0.1$ ns. For the case of calixarene mixed with naphthalene, the fluorescence spectrum shows that the band centered at 340 nm lies 2840 cm$^{-1}$ below the relatively broad 310 nm band found for calixarene crystals. The spectra also exhibit that the emission intensity increases with increasing calixarene concentration. The results are evident that the calixarene emission is quenched by the naphthalene. Phosphorescence of calixarene mixed with naphthalene crystals is observed to determine whether the emission is due to naphthalene. The phosphorescence peaks were compared with the ground-state vibrational frequencies of naphthalene and found to be in good agreement. The results indicate that inter-molecular energy transfer occurs between calixarene and naphthalene.

**Key words :** Luminescence, Energy transfer, Calixarene, Naphthalene

## Introduction

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] Solid state host-guest systems have provided much spectroscopic information about molecular properties. The lack of universal host material that forms single crystal and is a solid at room temperature has been a significant problem. It appears that calixarene may be the solution to this problem. 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 cone, partial cone, 1,2-alternate, and 1,3-alternate.[12-14] Calixarene has attracted researchers attention because it has remarkable chemical 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 compound 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.[14] 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] For these reasons, calixarene may serve as a universal host for spectroscopic studies and technological application of molecular solid guest-host system, but essentially nothing is known about the optical properties of these material, although some characteristics have been reported.[15-19]

Much of the previous photoluminescence works on calixarene has been done on porous silicon coated with calixarene,[15] on water-soluble calixarene,[16-18] or on Langmuir-Blodgett films.[19] Zhang and coworkers[15] studied the luminescence quenching effect for porous silicon coated with calixarene carboxylic acid derivatives. The experimental results demonstrate that calixarene can form thin films on the surface of Si. This yields a stable interface in aquous media demonstrating selectivity regard to photoluminescence quenching behavior dependent on the size of the calixarene. Carboxylic acid groups play an important role in the photoluminescence enhancement of porous silicon. Gravett and coworkers[17] reported the syntheses of a novel calixarene-containing monomer. Free radical polymerization of the calixarene containing monomer with 2-(6-sulfo-2-naphthoxy)ethyl methacrylate sodium salt resulted in a water-soluble polymer. The antenna polymers have proved interesting in attempt to mimic the processes involved in photosynthesis. These antenna polymers showed to solubilize various organic probe molecules, while the presence of the chromophore gives them ability to transfer energy absorbed by the polymer to solubilized probe molecules which can lead to the sensitized photochemical reaction of these solubilized probe molecules. They determined the location of the solubilized probe molecules within the polymer. Grady and coworkers[18] monitored the quenching of the fluorescence of chiral calixarene solution to determine the enantiomeric composition of chiral amines. They determined the enantiomeric composition of samples of (R)- and (S)-phenylethylamine and L- and D-norephedrine to within few percent. Nabok and coworkers[19] reported the formation and characterization of CdS nanoparticles in calixarene Langmuir-Blodgett (LB) films. They monitored UV-vis absorption

spectra to check the presence of CdS nanoparticles in LB film matrices. The experimental results demonstrated that the particle size does not depend on the type of calixarene or the number of LB layers.

Here we report the investigation of the photoluminescence for calixarene crystals as functions of temperature, time, and 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. This paper also report the observation of the energy transfer phenomena between calixarene and naphthalene from fluorescence decay and the sensitized phosphorescence. Naphthalene was chosen because a wealth of spectroscopic information has been accumulated on naphthalene molecules, and neat and mixed crystals of naphthalene.[20-28]

## Experimental Techniques

Calixarene crystals were prepared by slow cooling followed by slow evaporation of the solvent. After crysallization, the resulting crystals were rinsed with solvent. Naphthalene ($C_{10}H_8$) was purified by multiple (four times) recrystallization from ethanol, and zone-refined for 100 passes at a velocity of 1 inch/hour. To obtain mixture of calixarene with naphthalene, appropriate amount of naphthalene and calixarene were mixed and then dissolved using ethanol as a solvent. To determine whether the calixarene forms inclusion compound or not, *i.e.* naphtalene locate in the cavity of calixarene or between calixarene molecules, NMR spectrum was analyzed. The NMR spectrum shows that naphthalene locates between calixarene molecules.

The crystals were mounted between a quartz plate and in the closed cycled cryogenic system (APD CSW-202) to obtain the temperature between 12 K and 298 K. The excited states were generated by 325 nm radiation from a He-Cd laser (Liconix 3650N) or by 266 nm from 4th generation of pulsed Nd-YAG laser (SL825G, spectra laser systems). The emission was focused onto the entrance slit of a 0.85M double spectrometer (Spex 1403). The photosignal was
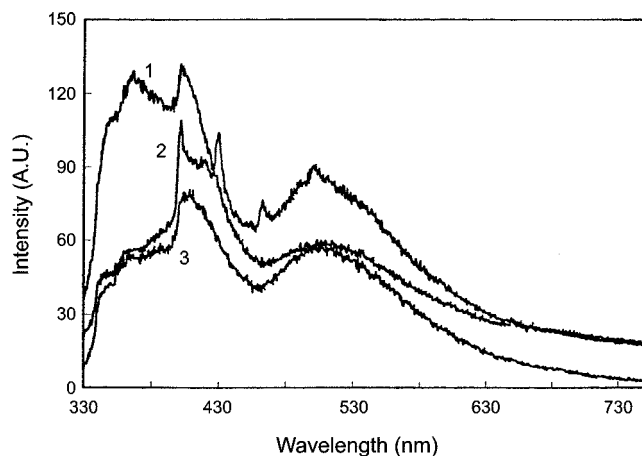


**Figure 1**. A set of steady-state luminescence spectra of calixarene crystals for different temperatures obtained with 325 nm excitation (1: at 298 K, 2: 12 K, 3: 298 K after annealing).
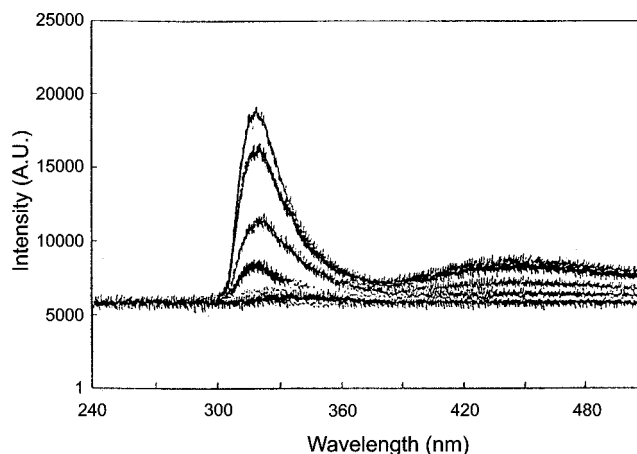


**Figure 2**. Time-resolved spectra of calixarene at 12 K for different delay times with excitation at 266 nm (increment of delay time is 1 ns).

detected with an a photomultiplier tube (Hamamatsu R943-02 GaAs) and amplified using a current amplifier at a gain of $10^8$ V/A. A photon counter was used for the time-resolved data acquisition. The time response of the electronics was tested with a pulse generator. All the experiments were controlled by a computer. The spectra were collected using an analog to digital converter.

## Experimental Results

A set of steady-state luminescence spectra of calixarene crystals for different temperatures obtained with 325 nm excitation is shown in Figure 1. 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 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.

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 1ns. The width and position of the band appear to be independent of the delay time. The linear semilog plot indicates that the time evolution of the fluorescence intensity of calixarene crystals is a simple exponential function of time. The life time was found to be $2.6 \pm 0.1$ ns. Delayed fluorescence was not detectable under the experimental condition used.

Steady-state fluorescence spectra of calixarene mixed with different concentrations of naphthalene obtained at 12 K with 266 nm excitation are shown in Figure 3. The spectra show that the broad band centered at 340 nm lies 2840 cm$^{-1}$ below the relatively broad 310 nm band found for calixarene crystals. The broad band contains the relatively sharp spectral features at 332 nm, 337 nm, 342 nm, and 352 nm
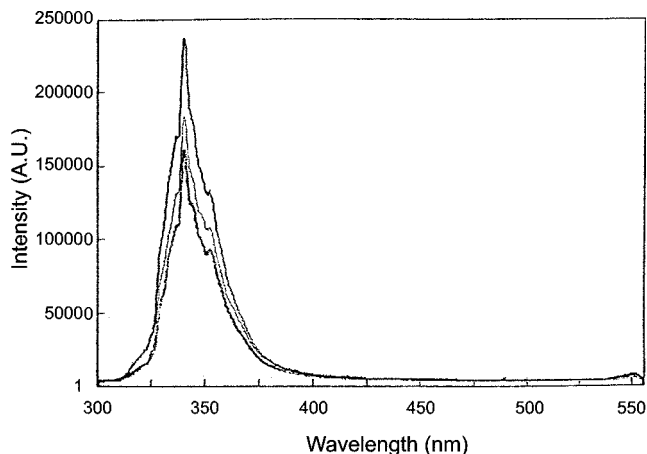
**Figure 3**. The fluorescence spectra of calixarene mixed with different concentrations of naphthalene obtained at 12 K with 266 nm excitation (the mole ratio of calixarene: naphthalene are top: 3 : 1, middle: 2 : 1, bottom: 1 : 1).
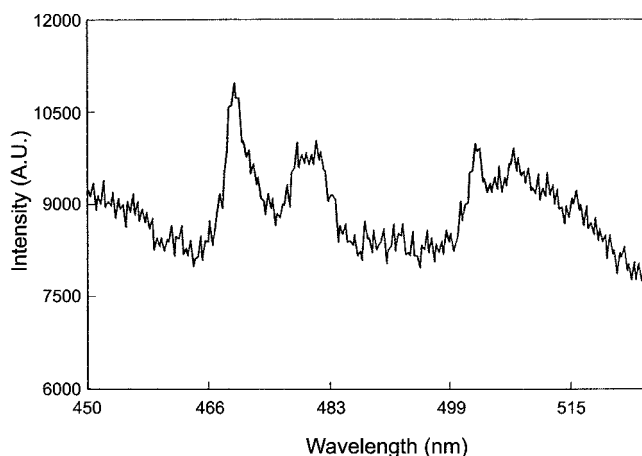


**Figure 4**. The phosphorescence of calixarene mixed with naphthalene obtained at 12 K with 266 nm excitation.

which is significantly different from that of calixarene shown in Figure 2. It is assumed that the emission of calixarene is quenched by naphthalene. The broad band presumably is due to a disordered structure. The spectrum also show that the increase of calixarene concentration results in an increase in the fluorescence emission of naphthalene. The results are evident that the calixarene emission is being quenched by the presence of the naphthalene.

The phosphorescence spectrum of calixarene mixed with naphthalene obtained at 12 K with 266 nm excitation is shown in Figure 4. The observed phosphorescence peaks appeared at 472 nm, 483 nm, 505 nm, and 510 nm. To determine whether the emission is due to naphthalene, the ground-state vibrational frequencies were compared with those for naphthalene and found to be in good agreement, assigned for $v_0$, $v_1$, $v_5$, and $v_7$, respectively.[29]

## Discussion

First, we consider the experimental results for calixarene

photoluminescence as a function of temperature. The experimental results, as shown in Figure 1, show significant changes in spectral features as temperature decreases from 298 K to 12 K. The spectrum obtained after increasing temperature from 12 K to 298 K (annealing), however, does not demonstrate the spectral features of the spectrum at 298 K obtained before annealing. The spectrun is similar to one at 12 K, but relatively broad which may be due to thermally activated dispersion. 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. 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 the structural transformation occurs during the annealing process.

The experimental results of time-resolved spectra of calixarene at 12 K demonstrate that 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 process 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.[30-32] 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 unimolecular decay processes 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 $2.6 \pm 0.1$ ns.

Now we consider the experimental results of calixarene mixed with naphthalene. Figure 3 shows the fluorescence spectra of calixarene mixed with naphthalene at 12 K obtained with 266 nm excitation. The spectrum shows that the broad band centered at 340 nm lies $2840$ cm$^{-1}$ below the relatively broad 310 nm band found for calixarene crystals. The broad band contains the relatively sharp spectral features at 332 nm, 337 nm, 342 nm, and 352 nm which is significantly different from that of calixarene crystals shown in Figure 2. It is assumed that calixarene emission is quenched by naphthalene. The broad band presumably is due to a disordered structure of calixarene. Calixarene can generally have four different conformations: cone, partial cone, 1,2-alternate, and 1,3-alternate.[12-14] Shinkai and coworkers[33] have shown that calixarene contains various ratio of mixture of four conformations depending on the experimental condition. In addition to these basic types of conformational isomers, there also be cases where the substituents are either inside or outside.[34] The disordered structure of calixarene would produce the spectral broad band. In order to determine whether the emission is due to naphthalene, phosphorescence of calixarene mixed with naphthalene was observed, as shown in Figure 4. The phosphoresnce peaks appeared at 471 nm, 483 nm, 505 nm, and 510 nm were compared with those for naphthalene and found to be in good agreement. These peaks correspond to the ground-state vibrational frequencies of naphthalene crystals, $v_0$, $v_1$, $v_5$, and $v_7$, respectively.[29] Therefore, we conclude that spectrum is attributed to emission of naphthalene, *i.e.* calixarene emission is quenched by naphthalene. Figure 3 also show the fluorescence spectra of calixarene mixed with different concentrations of naphthalene. The results demonstrate that increase of calixarene concentration results in an increase in the fluorescence emission of naphthalene. The result is evident that the calixarene emission is being quenched by the presence of naphthalene. In order to understand the concentration dependence of energy transfer, we consider the spatial distribution of naphthalene molecules among the calixarene molecules. Three possible configurations for the spatial distribution can be imagined: (A) separate phase of calixarene and naphthalene molecules, (B) stoichiometric mixture of calixarene and naphthalene with a separate phase of excess calixarene, and (C) calixarene with guest sites partially filled with naphthalene molecules, *i.e.* not all the available guest sites are occupied by naphthalene molecules. For configuration (A), energy transfer between calixarene and naphthalene is only possible at the phase boundaries. This situation would not produce a concentration effect on energy transfer. Configuration (B) would not show any concentration effect at all. The observed experimental results provide characteristic of a random distribution of naphthalene molecules and serve to identify the configuration (C).

## Summary and Conclusions

The luminescence of calixarene crystals has been studied as a function of temperature. The experimental results show that there are significant changes in spectral features as temperature decreases from 298 K to 12 K. The spectrum obtained after increasing temperature from 12 K to 298 K (annealing process), however, does not demonstrate the spectral features of the spectrum at 298 before annealing. The spectrum is similar to one at 12 K, but relatively broad which may be due to thermally activated dispersion. The experimental results reveal that a structural transformation from high temperature modification to low temperature modification occurs 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 no energy transfer processes occur and the depopulation of excited state density is mainly controlled by unimolecular decay processes dominating other decay processes. The lifetime of calixarene in the singlet excited state is found to be $2.6 \pm 0.1$ ns.

For the case of calixarane mixed with naphthalene, the spectrum shows that the broad band centered at 340 nm lies $2840$ cm$^{-1}$ below the relatively broad 310 nm band found for calixarene crystals. The broad band contain the relatively sharp spectral features which is significantly different from that of calixarene crystals. In order to determine whether the emission is due to naphthalene, phosphorescence spectrum of calixarene mixed with naphthalene crystals is observed. The phosphorescence peaks were compared with those for naphthalene and found to be in good agreement. The fluorescence spectra of calixarene mixed with different concentrations of naphthalene were observed. The experimental results demonstrate that increase of calixarene concentration results in an increase in the fluorescence emission of naphthalene. The result is evident that the calixarene emission is being quenched by the presence of naphthalene. Therefore we conclude that energy transfer takes place between calixarene and naphthalene. In order to understand the concentration dependence of energy transfer, the spatial distribution of naphthalene molecules among the calixarene molecules was considered. The observed experimental result provides characteristic of a random distribution of naphthalene molecules, *i.e.* calixarene with guest sites partially filled with naphthalene molecules, not all the available guest sites are occupied by naphthalene molecules.

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