Fluorescent Crystalloluminescence of *N*-Isopropylcarbazole

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Received: July 11, 2003; In Final Form: December 25, 2003

We have observed very bright visible luminescence from *N*-isopropylcarbazole (NIPCz) when the compound crystallizes from the molten state to a crystalline aggregate. The sample crystals were heated on a glass plate to above their melting point (380 K) and cooled gradually under ambient conditions. When their temperature fell below 350 K, sudden rapid crystallization took place, accompanied by bluish-white luminescence. Video imaging of the phenomena revealed that both the crystallization and luminescence occurred in the same time frame of <0.5 ms, demonstrating that the two effects were intimately related to each other, i.e., crystalloluminescence (XTL). Thermal analysis of the sample revealed that the preceding state prior to the crystallization was not a glassy solid, but a supercooled liquid state. The XTL spectrum agreed very well with both photo- and triboluminescence spectra of NIPCz. Moreover, its intensity was considerably higher than the reported values for other crystalloluminescent materials such as NaCl. This is the first demonstration of the fluorescent XTL of an organic material. We discussed the mechanism leading to XTL in detail on the basis of the available models, and we concluded that a valid explanation for XTL could be provided by triboluminescence mechanisms.

Introduction

Very weak visible luminescence is frequently observed when certain materials crystallize from a saturated solution or from the molten state. This luminescence is called crystalloluminescence (XTL), which was first reported for K_2SO_4 by Pickel in 1787.[1] XTL is a very intriguing phenomenon, because the light emission is coupled with a phase transition in the material, and it has attracted much attention over the last century.[2] However, the fundamental mechanisms underlying XTL are poorly understood, even now. So far, various materials have been reported to be crystalloluminescent: alkali halides, alkali sulfates, metal nitrates, water, and so on.[2] For these compounds, XTL can be observed upon crystallization from their aqueous saturated solutions. Among them, NaCl[3] and As_2O_3[4] have been the most rigorously investigated materials in terms of their spectroscopic properties, their dynamic behavior, the effects of impurities, the effects of stirring of the solutions, and so on. The interrelations between XTL and the photoluminescence (PL) of the material as well as the temporal evolution of XTL have also been investigated in detail. In addition to various experimental approaches, several groups have also reported theoretical models for the excitation mechanisms of XTL on the basis of nucleation theories.[5−7]

On the other hand, studies on XTL in organic substances have hitherto been limited to a few systems. To the best of our knowledge, only four reports have appeared, with each being published almost a decade apart. The first example was demonstrated for benzanilide by Safonov et al. in 1964,[8] and the second was reported for binary solution mixtures (acetone/acetonitrile, etc.) by Takeda et al. in 1973.[9] In 1982, Zink et al. reported the XTL spectrum of methyl salicylate.[10] In these cases,

it has been demonstrated that the XTL spectra are very similar to the corresponding PL spectra. In the fourth example, Koyanagi recently reported XTL behavior for 2-furaldehyde and benzaldehyde and asserted that these compounds showed luminescence with several different colors (bluish-violet, green, and yellow), although the spectra were not shown in the literature.[11]

All of the organic XTL-active compounds mentioned above are in the liquid phase at room temperature (i.e., neat oils), so that the XTL is induced by rapid cooling of the liquids; a vessel containing the liquid is immersed into liquid nitrogen. Therefore, the mechanisms leading to XTL have hardly been discussed in terms of the thermodynamics of the crystallization process. It is worth noting, furthermore, that the excited states of the XTL-active compounds reported previously possess (n, π^*) character, so the XTL spectra reported in the literature[8−11] are phosphorescent in origin rather than fluorescent. It is true that phosphoresce is much weaker in intensity than fluorescence and is likely to suffer from impurity and/or oxygen quenching. To obtain further insight into the excitation mechanism of XTL for organic substances, the XTL behavior of a fluorescent compound is worth studying in detail.

In the course of our study on the triboluminescence (TL) behavior of fluorescent *N*-isopropylcarbazole (NIPCz) crystals,[12] we observed a strong emission from NIPCz upon crystallization from its molten state (above room temperature), which should be classified as XTL. In this paper we report on a fifth example of an XTL-active organic compound and the first example of a fluorescent XTL compound. The XTL behavior of NIPCz crystals was revealed by means of both transient spectroscopic methods and thermal analysis, and the fundamental mechanism is discussed in relation to the triboluminescence (TL) of NIPCz.

Experimental Section

Commercially available NIPCz contains anthracene as an impurity that cannot be eliminated by usual purification

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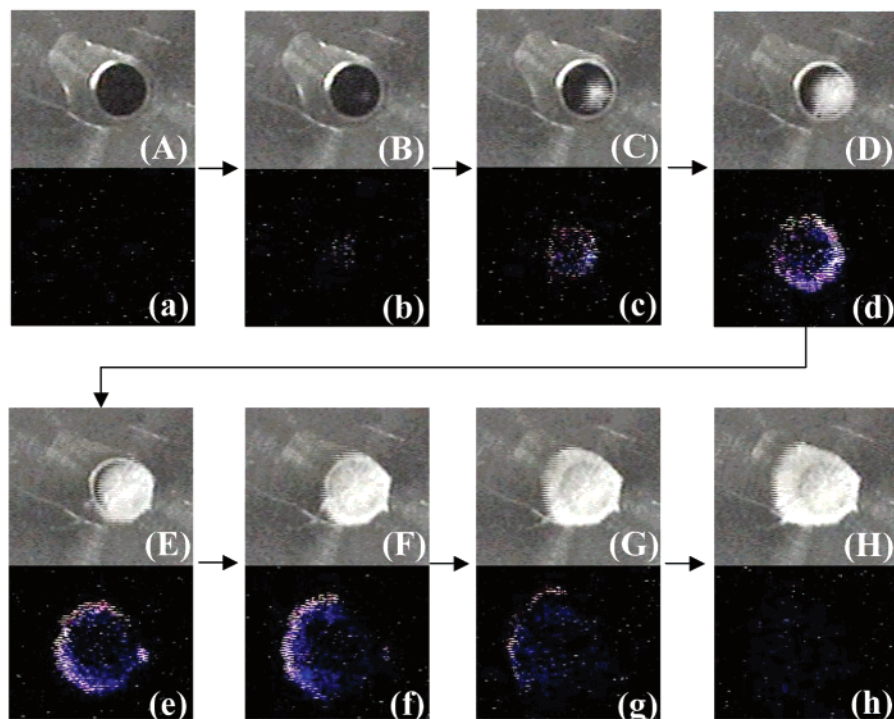‡ E-mail: kitamura@sci.hokudai.ac.jp.

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Figure 1. Successive video images of crystallization (upper row, (A)−(H)) and XTL (lower row, (a)−(h)) of NIPCz on a glass plate placed on a hot stage. The crystallization temperature was 330 K. Each image was taken at a video rate of 33 ms/frame. The data in the upper and lower rows were imaged under room light and in the dark, respectively. The hole (diameter = 2 mm) seen in the upper row is located just below the sample glass plate and used only for illumination. An illumination lamp in the hole was always turned off during the imaging. The hole did not affect this video observation. In the upper row ((A)−(H)), it is observable with the temporal evolution that the transparent oil (NIPCz in liquid phase) turns into the solid state (crystalline phase). Accordingly, emission of bluish-white luminescence is seen in the lower row ((a)−(h)). Both the crystallization and the luminescence occur in the same time frame.

methods.[13] Therefore, we synthesized and purified anthracene-free NIPCz according to the literature.[13] The melting point of the colorless needlelike NIPCz crystals was determined to be 383 K by using a micro-melting-point apparatus (Yanaco, MP-500D). Because the melting point of NIPCz is much higher than room temperature, the rapid cooling method mentioned above was not applicable to XTL. Therefore, the following method was employed in the present experiments. A NIPCz sample (∼1 mg) was placed onto a glass plate and was heated to 390 K using the MP-500D. The molten sample (oil) was then gradually cooled under ambient conditions (cooling rate; 10 K/min) to induce crystallization.

The crystallization and XTL behavior were visualized using a video camera (Sony, CCD-TRV91). The spectra and the transient intensity of the XTL were measured with a multichannel photodiode array detector (Hamamatsu, PMA-11) and a photomultiplier tube (Hamamatsu, R928)−digital storage scope (500 MHz, Recroy, 9354C) system. A nanosecond-pulsed Nd^{3+}:YAG laser (Spectra Physics, Pro-250-30, fwhm ∼ 10 ns at 355 nm) and a picosecond-pulsed blue laser diode (picoQuant, PDL400, fwhm ∼ 50 ps at 400 nm) were employed to calibrate the system. The fluorescence (PL) lifetime of the NIPCz crystals was measured using a time-correlated single photon counting technique, whose details are reported elsewhere.[14] The harmonic output from a Ti:sapphire laser (λ_{ex} = 300 nm) was used as an excitation light source. Thermal analysis of the crystallization was carried out using a differential scanning calorimeter (Seiko, DSC200).

Results and Discussion

Visualization of XTL. Under the present experimental conditions, rapid crystallization of the NIPCz took place in the

temperature range 310−350 K, which is lower than the melting point of the crystal (383 K). The crystallization was accompanied by the emission of bluish-white light, as easily confirmed in the dark by the naked eye. The upper row in Figure 1 ((A)−(H)) shows some video images of the crystallization process that were recorded under room light, whereas the lower row in the figure ((a)−(h)) exhibits those for which XTL behavior was accumulated in the dark. The images were taken at a video rate of 33 ms/frame. A hole seen in the upper row was located just below the sample glass plate and used only for illumination to observe the melting of the crystals (a lamp in the hole was always turned off in the experiments). Just before crystallization (Figure 1A), the NIPCz sample is seen as an oil, i.e., the molten state of NIPCz. After 33 ms (video rate), a faint white spot appears, as seen in Figure 1B. Because light is scattered by the sample, this corresponds to the crystallization of NIPCz. With time, the crystallization of the sample becomes obvious, as seen very clearly in images (C)−(H). On the other hand, the lower row in the figure demonstrates that the crystallization accompanies the bluish-white emission from the sample, (b)−(g). The present observations directly indicate that the crystallization and XTL behavior correlate very well with each other. Also, the results demonstrate that the crystallization has been completed within <0.3 s, and therefore the duration time of XTL is <0.3 s under these experimental conditions. This behavior was well reproducible, except for the crystallization temperature. In many cases, the crystallization temperature was ca. 330 K and crystallization was rarely observed just below the melting point of 370−380 K.

DSC Analysis. The crystallization temperature of NIPCz was always lower than the melting point, as described above. Therefore, the oil-like state just before the crystallization should
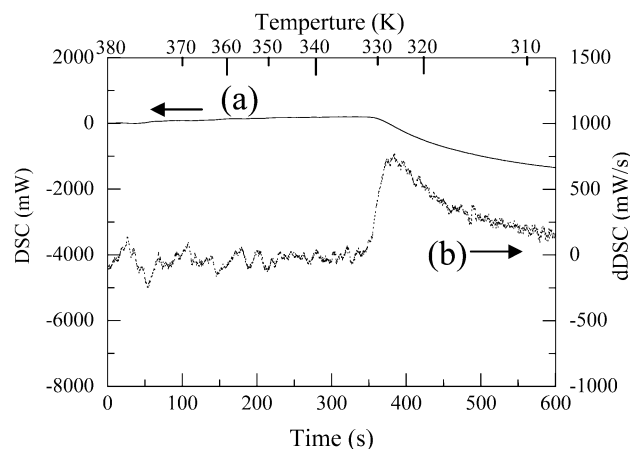
Figure 2. DSC (a) and *d*DSC (b) curves of NIPCz measured by cooling from the melting point. The cooling rate was 9 K/min (almost the same as that used for the imaging, Figure 1). The exothermic peak around 330 K corresponds to crystallization.

be either a supercooled liquid or an amorphous glassy solid. Although glassy solid states are commonly observed in polymers, it was recently reported that low molecular weight molecules such as a chlorobenzene/toluene binary mixture formed glasses.[15] To check this point, we carried out DSC measurements. In DSC measurements *with increasing temperature*, the heat of crystallization of NIPCz was evaluated to be 17.7 kJ/mol. Figure 2 shows the DSC (Figure 2a) and differential DSC (*d*DSC, Figure 2b) curves of NIPCz. The *cooling* rate was set at ca. 9 K/min (380−320 K), which was a value similar to that used for the experiments in Figure 1. An exothermic peak was seen clearly at 330 K, and this temperature agreed very well with the crystallization temperature of NIPCz as observed by the imaging experiments (i.e., Figure 1). Therefore, we conclude that the exothermic peak in Figure 2 is due to the heat of NIPCz crystallization. Above 330 K (before crystallization), it is worth noting that no significant exothermic or endothermic peak is observed in both the DSC and *d*DSC curves. Generally, a glass transition of a material is reflected in a DSC curve as a shift of the baseline. The present results therefore indicate that a glass transition from a supercooled liquid state to a glassy solid state does not occur before the crystallization. Thus, we conclude that the NIPCz crystallization accompanying the XTL takes place from a supercooled liquid state.

XTL Spectra. Figure 3 displays the XTL spectrum of the NIPCz, together with the relevant fluorescence (PL) spectrum. This XTL spectrum was obtained from one event of crystallization. Although the S/N ratio might not necessarily be considered to be high enough because only a single measurement was made, an emission spectrum with a maximum at 390 nm was successfully observed. The XTL spectrum was almost identical to the PL spectrum of the NIPCz crystals. In related studies in the past, it was reported that XTL events sometimes accompanied emission from an impurity other than that from the XTL-active compound itself.[3,4] However, in the present experiments, no phosphorescence at all was detected from the NIPCz ($\lambda_{max} \sim 500$ nm).[16] It is worth noting, furthermore, that Takeda et al. investigated XTL from a binary mixture (methylbutyl ketone/dimethylacetamide) doped with oxazole derivatives (POPOP, etc) as a fluorescence sensitizer.[9] In this case, neither fluorescence nor phosphorescence was detected from the oxazole derivative in the XTL spectrum of the binary mixture. Therefore, to the best of our knowledge, this is the
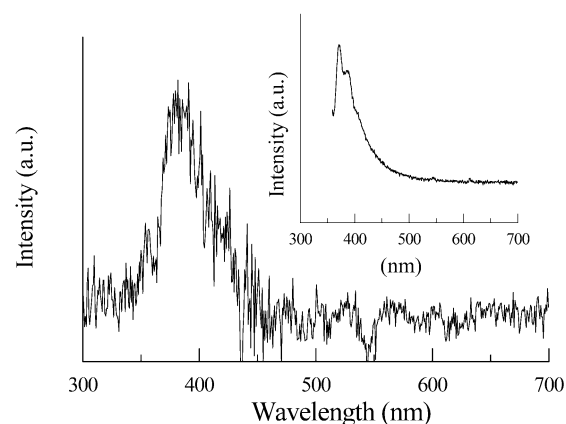

Figure 3. XTL spectrum of NIPCz measured for a single crystallization event. The fluorescence (PL) spectrum obtained by excitation at 355 nm is also shown in the inset.
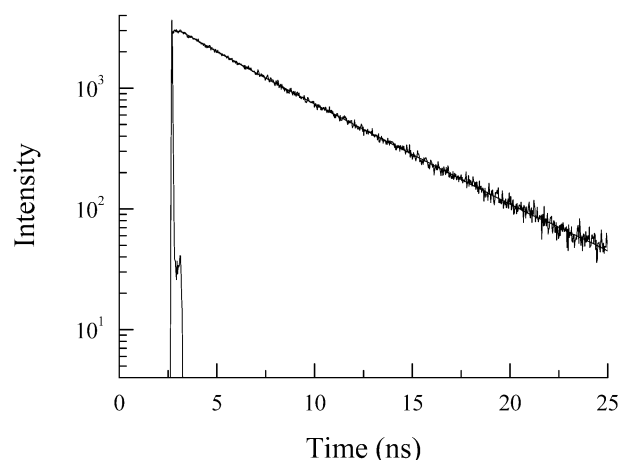

Figure 4. Temporal evolutions of the XTL of NIPCz observed over both long ((a), upper panel) and short ((b), solid line in the lower panel) time scales. The noise level of the apparatus that we used is also shown (lower trace in (a)). The response function of the apparatus is shown as the dotted line in (b), which is the trace of the output from a picosecond-pulsed blue laser diode (fwhm $\sim$ 50 ps at 400 nm).

first report of fluorescent crystalloluminescence from an organic compound: NIPCz.

It is worth pointing out that some carbazole derivatives produce an excimer in the condensed phase, as confirmed by characteristic broad and structureless fluorescence around 400−450 nm.[17] However, the XTL spectrum of NIPCz could best be assigned to monomer fluorescence. For excimer formation, two carbazole rings must take a sandwich-like orientation (i.e., a face-to-face geometry). In the crystalline phase of NIPCz, two adjacent carbazole rings take a perpendicular orientation,[18] so an excimer cannot be produced in the crystals owing the poor π-electronic overlap between the molecules.

Transient Intensity of XTL. To understand the fundamental mechanisms of XTL, it is very important to reveal its temporal evolution. Figure 4 shows temporal evolutions of the XTL of NIPCz observed over both long and short time scales. In the long-time regime (Figure 4a), a lot of flash-like emissions are detected over the temporal window at <0.4 s. This is almost consistent with the results in Figure 1, where both the XTL and the crystallization occur within ca. 0.3 s. The XTL of NaCl[3] and As$_2$O$_3$[4] exhibit quite complicated temporal behavior in the time frame from minutes to submicrosecond. In the case of the XTL observed for the crystallization of NaCl from a saturated solution, the total time scale of crystallization (precipitation) is
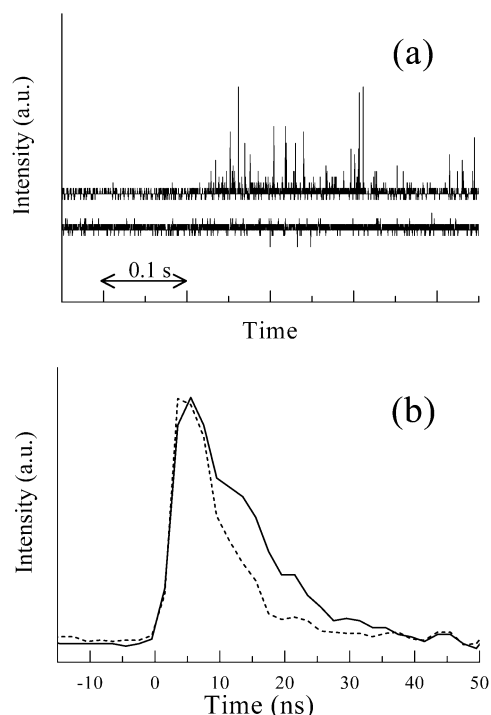
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Figure 5. Fluorescence decay profile of NIPCz crystals monitored at 370 nm. The profile can be well fitted with a biexponential function whose main time constant is 5 ns.

on the order of $<10^3$ min, indicating that the duration time of the XTL is of the same order. By contrast, because the crystallization of NIPCz takes place from the nonequilibrium supercooled liquid state, both the crystallization and the XTL proceed very rapidly, on the order of $\sim$0.3 s.

The time evolution of the present XTL is characterized by the appearance of flash-like emissions. Flash-like emissions have been also reported for the XTL of NaCl.[3,19] For instance, Garten and Head investigated the influence of an impurity (Ag^+, Pb^{2+}, etc.) on the temporal evolution of XTL of NaCl in the submillisecond regime[3] and found a pulse train composed of numerous flash-like emissions. They concluded that the flashes were generated by the formation of a crystal nucleus and that the number of flashes could correspond to the number of crystal nuclei. Because the total duration time of the present XTL ($\sim$0.3 s) shows a good correlation with the video data in Figure 1, we also consider that each of the flashes originated from the formation of a crystal nucleus of NIPCz.

To obtain further information, we investigated the temporal profile of an individual flash. The results are shown in Figure 4b, together with the response function of our detection system. The duration time of an XTL flash was very short, and the time profile almost traces the response function. Taking the response function into account, we estimated the decay time of the XTL flash to be ca. 5–10 ns. The fluorescence lifetime of the present NIPCz crystals, as determined by a single photon counting technique, was 5 ns, as shown in Figure 5. The decay times of the fluorescence and the XTL flash roughly agree with each other. This also supports the theory that the XTL of NIPCz is fluorescent in origin. Furthermore, the results suggest that the excitation process of an individual XTL flash occurs in a very short time scale compared with the decay time, probably on the order of <1 ns.

The intensity of an individual flash emission was independent of the amount of sample used (1–10 mg). This may also support the idea that the flash emission originates from the formation

of a single NIPCz crystal nucleus. Furthermore, such circumstances enable us to estimate the number of photons emitted from an individual flash on the basis of data analogous to that in Figure 4b. The photomultiplier tube used was then calibrated by employing 355 nm laser pulses (fwhm $\sim$ 10 ns) with various energies, as determined by a joule meter. The use of the 355 nm laser pulses was convenient, because the wavelength and pulse width of the laser output were very close to those of the XTL flash. By comparing the intensities of individual flashes with that of the calibration data, we estimated the number of photons to be $\sim$10^{12} photons/flash. This value is considerably higher than that reported for the XTL flashes of NaCl, which was 10^4 photons/flash.[19] Namely, the XTL of NIPCz is very bright; indeed, it is probably the most intense XTL ever reported.

XTL Mechanisms. The XTL mechanisms proposed so far fall into three categories:[2] (i) excitation by the energy released by crystalline modifications, i.e., polymorphic transition, (ii) excitation by a process analogous to that of chemiluminescence, and (iii) excitation by fractures and cracking of crystals as they grow, i.e., triboluminescence (TL). On the basis of the present experimental results, we discuss the possible excitation mechanisms of NIPCz, as follows.

Mechanism i has been proposed for the XTL generated during the precipitation of As_2O_3 from an aqueous solution. A solid– solid phase transition accompanied by lattice rearrangements releases energy that can excite a crystal. Indeed, As_2O_3 crystals can take two phases; monoclinic and cubic geometries.[6] Crystalline modification from the former to the latter accompanies the XTL. Theoretical modeling was developed by Chandra on the basis of a homogeneous nucleation theory and precipitation kinetics.[6] His model explained the XTL behavior of As_2O_3 very well by assuming a thermal population of the excited states by readjustment of the atoms and subsequent XTL excitation by the energy released during the polymorphic phase transition. On the other hand, NIPCz has one crystal phase, whose space group is orthorhombic, *Iba*2.[18] Also, DSC analysis of NIPCz (Figure 2) indicates that phase transitions other than crystal melting do not occur in the crystals. Therefore, we consider that the polymorphic mechanism (i) can be neglected as a source for the excitation of XTL in NIPCz. In relation to mechanism i, the thermal excitation of NIPCz by the heat of crystallization should be also considered. However, the heat obtained (17.7 kJ/mol) is apparently insufficient to produce the excited singlet state (S_1) of NIPCz.

As an analogous model to mechanism i, Ring very recently reported a new theory (population balance theory), focusing on the role of the nucleation of nanosized clusters.[7] He suggested that collisions of clusters produced activated states during the phase transition and that the relaxation of the activated states to the ground state could excite XTL. He also pointed out that the intensity of XTL depended on the frequency of these collisions. In the present case, crystallization takes place rapidly in the neat liquid with concentrations of NIPCz as high as $\sim$10 M. Therefore, the frequency of cluster collisions would be higher than that for the XTL of As_2O_3, resulting in the bright XTL of NIPCz. Such a mechanism is presumably partly involved in the excitation of XTL in NIPCz.

Mechanism ii, which describes XTL as a kind of chemiluminescence, is based on experimental results on the enhancement of the XTL of NaCl and As_2O_3 by the addition of a foreign molecule such as HCl, metal ions, or peroxides.[3,4,20] In this model, recombination of the ions or defects is considered to excite the XTL. However, this chemiluminescence mechanism

(ii) can apparently be precluded because the present XTL is observed for the pure neat liquid.

The most plausible dominant processes for the XTL of NIPCz are those that occur in mechanism iii. In this mechanism, XTL is explained by the formation of microcracks and subsequent fracture of embryo crystals during a phase transition, similar to the TL mechanism. It is worth emphasizing that most of crystalloluminescent compounds also show triboluminescence.[21] Actually, organic XTL-active compounds such as benzanilide and methyl salicylate are TL-active and the XTL spectra agree well with the relevant TL spectra. As reported previously, the TL spectrum of NIPCz coincides with the relevant PL spectrum,[13] and therefore also with the XTL spectrum. One of the important results in the present study is that the XTL of NIPCz is very intense. This is also consistent with the very high TL activity of the compound.[13] Furthermore, Trautz et al. have pointed out that, because the XTL intensity increases with the increasing rate of crystallization, the TL mechanism explains very well the XTL mechanism.[21] In rapid crystal growth, crystals suffer from higher internal strains compared with those formed at slower growth rates. When crystals are triboluminescent, the higher crystal strains due to the higher crystallization rate bring about more efficient crystal fracture, leading to more intense TL. This is what we have observed in the present experiments, though the data obtained under slow crystallization conditions are not shown here. Fracture of the crystals generates highly charged new surfaces followed by charge recombination or electric discharge that lead to the excitation of NIPCz molecules. At present, it is rather difficult to measure the internal strain during the crystallization, and also to confirm the generation of electrons or ionic species (cation and anion of NIPCz). We are currently carrying out acoustic measurements to evaluate the internal strain and also diffuse reflectance spectroscopy to detect the ionic species. Anyhow, all of the experimental results for NIPCz, including the present observations, the TL activity, and the crystal structures, indicate that the TL mechanism (iii) is the most plausible and valid model for the XTL excitation of NIPCz.

Such a conclusion does not contradict that for the XTL mechanism in other XTL-active compounds that have been reported so far. Furthermore, Garten and Head have reported that the energy released by polymorphic or phase transitions (mechanism i) is insufficient for the excitation of XTL in an organic compound.[22] In some cases, the TL spectrum of an inorganic XTL-active compound is different from the relevant XTL spectrum, and then mechanism i might be the principal reason for XTL of an inorganic compound. At the present stage of investigation, the XTL of an organic compound is best described by the TL mechanism (iii).

Concluding Remarks

In the present work, we found very bright luminescence from NIPCz when the compound crystallizes from the molten state (i.e., XTL), as observed by the naked eye. The temporal profiles of the XTL and the observed video images of the crystallization process corresponded very well with each other, demonstrating that the luminescence originated from the phase transition from the molten state (supercooled liquid) to the crystalline state. The most important result is that the present spectroscopic studies demonstrated that the XTL of NIPCz was fluorescent in origin, which is the first example of this phenomenon ever reported among XTL-active organic compounds. Furthermore, our rough estimation indicated that the intensity of the XTL flashes was 10^8 higher than that of an inorganic XTL-active compound (NaCl); i.e., it is the brightest XTL-active compound. The XTL activity of NIPCz was correlated with the TL activity, and the XTL of the compound was best explained by the TL mechanism. Besides NIPCz, we have reported that *N*-ethyl-3-ethylcarbazole and *N*-ethyl-3-vinylcarbazole are triboluminescent. Therefore, systematic studies on these carbazole derivatives would provide further detailed information on the correlation between the XTL and TL activities, which is the next step in the study and which is currently in progress.

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