Decomposition of unpolarized fluorescence spectrum of uniaxially oriented 1,3,5-triphenylbenzene microcrystals into polarized fluorescence spectra

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Abstract

Luminescence from solids such as crystals and aggregates is of growing academic and industrial interest. In this study, we report decomposition of the unpolarized fluorescence spectrum of uniaxially oriented 1,3,5-triphenylbenzene (TPB) microcrystals into four polarized spectra measured with polarizer (V: vertical and H: horizontal) and analyser (V: vertical and H: horizontal), where V and H indicate perpendicular and parallel to the layer of TPB molecules in the crystal, respectively. Resolved spectra were interpreted in terms of the molecular and excimer like (J- and H-dimer) emissions. The origin of the excimer like emissions was discussed in relation to the molecular packing in the crystal. It was shown that polarized crystal fluorescence can provide insight into the excitation/emission process in the crystal. Although preliminary, this study demonstrates the potential of polarized fluorescence to elucidate the luminescent mechanism.

1. Introduction

Recently, luminogenic compounds have been attracting attention in various applications such as organic light-emitting diodes[1]. In particular, compounds that emit light in the solid state are of great interest as aggregate-induced emission (AIE)[2–11] and crystallization-induced emission enhancers (CIEE)[12, 13]. Understanding the emission mechanism in the crystalline state is essential to improve the emission mechanism of crystals. For example, time-resolved measurements might be useful for elucidating the dynamics of excited states and the emission mechanism[14]. Also, the measurement of fluorescence anisotropy is important for understanding anisotropic molecular interaction in crystals[15]. Single crystals are the most suitable to measure crystal fluorescence because the crystal anisotropy is lost if powder crystals are used, but a single crystal of a size suitable for measurement is difficult to prepare. This paper reports the polarized fluorescence of 1,3,5-triphenylbenzene (TPB) microcrystals.

TPB has been studied in various fields. Environmental and chemical studies have been reported[2, 16–21], including not only in solution but also in solid state, columnar liquid crystalline state[19], hole transport matrix[20], and organometallic skeleton[21]. Its crystallographic structure is known[22]. Therefore, TPB is a good choice for studying fundamental aspects of fluorescence anisotropy. Although TPB can form large single crystals[23], magnetically oriented TPB microcrystals were used in this study so that the crystal axis is aligned in one direction with respect to the consolidating solid matrix. The magnetic technique is of great help when we only have microcrystals under investigation.

In this study, the unpolarized spectrum was decomposed into anisotropic spectra by measuring with polarizer and analyzer. It was shown that fluorescence due to intramolecular interaction masked by monomer fluorescence was clearly resolved.

2. Experimental
2.1. Sample preparation of a magnetically oriented microcrystal array

A few microcrystals having well-defined shape were chosen from a TPB sample (Tokyo Chemical Industry Co., Ltd., Tokyo) and immersed in an ultra-violet (UV) curable monomer (XVL14 of Kyoruisu Chemical, Tokyo, Japan) contained in a plastic straw of 6 mmφ. The straw was set horizontally in a horizontal magnetic field (1 T) generated by an electromagnet, where the straw axis was perpendicular to the magnetic field. The straw was rotated about its long axis at two different rotating speeds, 5 and 50 rpm which were switched every 90°. After exposure to the magnetic field for about 20 min, the UV light was irradiated to consolidate the crystal orientation[24]. Then, the straw was peeled off to obtain the crystal/resin composite for spectroscopic measurements (see Fig. 1). Under this experimental setting, the hard magnetization axis $\chi_3$ of the TPB crystal, which corresponds to the crystallographic a axis, is aligned parallel to the straw axis[25].

2.2. Fluorescence measurements

Fluorescence spectra from prepared samples were measured by a fluorescence spectrophotometer (Perkin Elmer, LS55) with polarizer and analyzer. The excitation was performed at 300 nm. The optical system setting for polarized fluorescence measurement is shown in Fig. 1.

3. Results And Discussion

As shown in Fig. 1, the sample excitation is performed horizontally (H), vertically (V), or without polarizer (N), and the emission is measured horizontally (H), vertically (V), or without analyzer (N). Four combinations of the directions of polarizer and analyzer are denoted by VV, VH, HH, and HV, where the first and the second symbols indicate the directions of polarizer and analyzer, respectively, in addition to the combination of Ns denoted by NN.

The crystal system of TPB is orthorhombic ($Z = 4$) and the relationship between the magnetic and crystallographic axes is $\chi_1 \parallel c (11.22\text{Å}), \chi_2 \parallel b (19.36\text{Å})$ and $\chi_3 \parallel a (7.55\text{Å})[24, 25]$. The $\chi_1$ and $\chi_3$ axes are referred to as easy and hard magnetization axes, respectively. The $\chi_3$ axis aligns parallel to the sample (or magnetic field) rotating axis. Therefore, in the rod-shaped sample, the crystal a axis aligns parallel to the rod axis, i.e., parallel to the vertical direction (V) of the polarizer and analyzer. In the crystal, TPB molecules are stacked in a layer (bc plane). This molecular layer is parallel to the H direction.

Since two different sample rotation speeds were employed for sample preparation in the magnetic field, it was expected that the a axis of the crystal would align in a specific direction[13]. However, very weak angular dependence of the spectral shape was observed when the sample was rotated about the rod axis. This indicates that the crystals in the rod sample exhibit uniaxial orientation of the a axis under the current experimental condition of sample preparation. In the analyses that follow, we consider the sample
as uniaxial although we cannot rule out the possibility that the a and b directions are spectroscopically very close.

Figure 2 shows the fluorescence spectra of aligned microcrystals, NN, VV, VH, HH, and HV, along with the solution spectrum (Soln). The intensity of the spectrum is normalized at the peak top; the only the peak shape matters. The spectra show fine noises that are attributed to machine noise. The broad peaks are clearly distinguished from each other. This difference in spectral shape is a result of complicated processes including excitation and emission.

The transition probability is proportional to the transition moment \( m = \int \psi_i^* \mathbf{H} \psi_f \, d\tau \), where \( i \) denotes the initial state and \( f \) denotes the excited state by Hamiltonian \( H \) of the irradiating light. Given \( \psi_i \) and \( \psi_f \), we have \( m = 0 \) or \( m \neq 0 \) according to the polarization of light. Therefore, it is evident that the polarity of the excitation affects the spectral shape. On the other hand, the process of internal transfer and the subsequent emission is unknown, making difficult to understand the resulting fluorescence spectra.

The NN spectrum is broader than that of Soln due to the intermolecular interactions in the crystal. The HV spectrum is closest to the Soln, indicating that HV is mainly due to molecular emission. It also exhibits a slight additional emission at 420 nm, which may be attributed to the intermolecular interaction. VH and HH spectra are close. This indicates that the H emission process is similar irrespective of the excitation and internal transfer process. In contrast, VV and HV spectra exhibit large difference. Especially, VV exhibits emissions at shorter and longer wavelengths. This indicates that the V emission process strongly depends on the preceding excitation and internal transfer process.

The NN spectrum is the contribution of the four polarization emissions, VV, VH, HH, and HV. Then, it will be decomposed into the four spectra, enabling quantitative analyses. The NN spectrum was decomposed into VV, VH, HH, and HV spectra. Weighting factors \( k_{VV} \), \( k_{VH} \), \( k_{HH} \), and \( k_{HV} \) were determined so that the difference is minimized between the area of the NN and the weighted sum of each peak area, i.e., \( S_{NN} - (k_{VV} \times S_{VV} + k_{VH} \times S_{VH} + k_{HH} \times S_{HH} + k_{HV} \times S_{HV}) \), where \( S_{NN}, S_{VV}, \) etc. are the areas of each peak. The optimized values were \( k_{VV} = 0.097, k_{VH} = 0.134, k_{HH} = 0.138, \) and \( k_{HV} = 0.631 \). The result is shown graphically in Fig. 3. The solid black line is NN and the broken line is the weighted summation. The calculated result reproduces the NN spectrum well.

The contribution of the HV is the largest. HV is mainly contribution of the intramolecular process, as was previously discussed. Therefore, the NN spectrum is mainly composed by the intramolecular emission. The spectral shapes of VH and HH are similar, as discussed previously. The intensities of these two spectra are almost the same. In the present decomposition procedure, a reliable decomposition of VH and HH is difficult to obtain because the spectral shapes of these two are almost identical. Therefore, the result of \( k_{VH} \approx k_{HH} \) is just tentative. The intensity of the VV spectrum is the lowest.

The current decomposition is not perfect because the microcrystal sample under consideration is aligned only uniaxially. Further understanding of crystal anisotropy of fluorescence can be made by the
measurements of H/V emission from the a, b, and c crystal axes upon H/V excitation from the respective crystal axes.

Figure 4 shows the molecular packing of TPB molecules in crystal. The front view shows that the molecules are arranged face-to-face, indicating the presence of H-dimers. Viewed from the side, molecules are arranged head-to-tail, indicating the presence of J-dimers. Both H- and J-dimers exist in the TPB crystal.

Scheme 1 shows the energy and transition diagram for the H-dimer and J-dimer. From this scheme, we find that the H-dimer is responsible for the blue-shift, and the J-dimer for the red-shift. This scheme can explain the blue- and red-shift observed in the VV, VH, HH, and HV polarized fluorescence spectra (Fig. 2). In particular, the red-shift at 450–500 nm and the blue-shift around 350 nm to 330 nm pronounced in VV can be explained by J-dimer and the H-dimer, respectively.

4. Conclusions

The polarized fluorescence spectra of uniaxially oriented microcrystals of TPB were measured using polarizers (H and V) and analysers (H and V). The unpolarized spectrum measured without polarizers or analysers (denoted as NN) was resolved into four components: VV, VH, HH, and HV, where the direction H corresponds to the molecular layer in the crystal. The HV component was dominant and the VV component was the smallest. The spectrum shape of HV was similar to that of the solution and assumed to be a single molecule emission; the VV spectrum showed significantly large blue- and red-shift peaks that are attributed to the H- and J-dimers assumed in the crystal, respectively.

In this study, we have shown, albeit preliminary, that polarized fluorescence has the potential to elucidate the luminescence mechanism. We are currently conducting single crystal fluorescence measurements to further explore the potential of polarized fluorescence.

Declarations

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Conflicts of Interest

There are no conflicts of interest to declare.

Ethical Approval

Not applicable as the study does not include any use of animals and humans.
Competing interests

The authors declare they have no competing interests.

Authors' contributions

Michihiro Hara contributed to the data collection. Experimental was done by Michihiro Hara.

Tsunehisa Kimura and Tatsuya Takeshita participated in data analysis. Hiroyuki Kurata contributed to providing helpful information and suggestion of the compounds. All authors contributed to the results discussions. The manuscript was written and revised by all authors. All authors read and approved the final manuscript.

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Availability of data and materials

All data analyzed in this study are included in this paper and raw data are available to the corresponding author upon reasonable request.

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**Scheme 1**

Scheme 1 is available in the Supplementary Files section.

**Figures**

**Magnetically oriented TPB microcrystal in the rod**

![Image of a magnetically oriented TPB microcrystal in a rod with a polarizer and analyzer](image)

**Figure 1**

Optical setting of anisotropic fluorescence measurements for a magnetically oriented microcrystal of TPB (photograph in the middle). H and V indicate the two directions, horizontal and vertical, respectively, of polarizer and analyser. In the rod sample (diameter of 6 mmf), the hard magnetization axis ($\chi_3 \parallel a$ axis) of the microcrystals is aligned in the direction of the rod axis. The $a$ axis coincides with the direction perpendicular to the molecular layer.
Figure 2

Fluorescence spectra, NN, VV, VH, HH, and HV of aligned microcrystals of TPB (solid curves) and solution spectrum, Soln (dotted curve).
Figure 3

The decomposition of fluorescence spectra of NN into VV, VH, HH, and HV. The weight factors are $k_{VV} = 0.097$, $k_{VH} = 0.134$, $k_{HH} = 0.138$, and $k_{HV} = 0.631$ for VV, VH, HH, and HV, respectively. The data between 340 nm and 550 nm were used. Baselines of each spectrum were corrected at 550 nm before the decomposition.
Figure 4

Molecular packing of TPB molecules in crystal. Crystallographic data (CSD Entry: TPHBEN01, 1275258) was obtained from Cambridge Structure Database Center.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- Scheme1.png