

Formation and Properties of Organic Long Persistent Luminescence Crystals Containing Benzidine Derivatives by Melt Crystallization

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Abstract

Organic molecules that exhibit long persistent luminescence (LPL) are rapidly gaining attention for a variety of applications. In this study, organic molecules with simple structures were selected and organic long persistent luminescence (OLPL) crystals were prepared. The crystal structure of the prepared OLPL crystal was elucidated and the guideline for the design of OLPL crystal was clarified. LPL was observed in OLPL crystals prepared with TMB as the guest molecule and 1,2-bis(diphenylphosphino)ethane as the host molecule. XRD measurements of the OLPL crystals suggest that the guest molecule is a solid solution substituted in the stable crystal structure of the host molecule in a lattice-shrinking direction.

Keywords

Melt Crystallization, Host-Guest Chemistry

1. Introduction

Materials that exhibit long-lasting luminescence (LPL) are used in glow-in-the-dark clock dials and emergency guide lights because they accumulate ultraviolet and visible light and continue to emit light for several hours [1]. LPL materials are mainly composed of inorganic materials. In the mid-1990s, LPL materials using strontium aluminum oxide (SrAl_2O_4) doped with europium and dysprosium were developed [2]. LPL materials, which are composed of inorganic materials, have been widely used due to their long lifetime of more than 10 hours and high durability. Organic long-lasting light-emitting materials can be easily synthesized in large quantities and are soluble in solvents, so they can be coated. In addition, because of the ability to easily control luminescent colors based on the molecular

structure, they are expected to be used in applications such as paints, biomarkers, and display devices, and are rapidly attracting attention. Recently, organic guest/organic host systems using electron donors and acceptors, organic guest/inorganic host systems, and microcrystalline systems have been proposed to increase the sustainability of light emission [3]-[11]. In model guest/host system, N,N,N',N'-tetramethylbenzidine (TMB), a strong electron-donating molecule and has a very stable radical cation, was selected as the donor molecule, while the acceptor molecule was 2,8-bis(diphenylphosphoryl)dibenzo [b,d] thiophene (PPT), a strong electron accepting molecule has been selected [3] [7]. The mechanism of LPL development in this model guest/host system has been vigorously studied. However, the crystal structure of OLPL crystals has not been elucidated in detail due to the very low guest-molecule ratio and the complex structure of the organic molecules used. Therefore, in this study, we independently selected organic molecules and fabricated OLPL crystals. The crystal structure of the prepared OLPL crystals was elucidated and the design guidelines for OLPL crystals were clarified.

2. Experimental

2.1. Fabrication of OLPL Crystal Film

The OLPL crystal films were prepared by melting crystallization as shown in **Figure 1**. A heat resistant petri dish was placed on a hot plate and a quartz substrate was placed on top of it. A mixture of Guest and Host molecules was placed on a quartz substrate and heated to 200°C for about 10 seconds. After melting, a quartz substrate was placed over the top and rapidly cooled to room temperature. The Guest/Host ratio was Guest: Host = 0 mol%: 100 mol%, 1 mol%: 99 mol%, 10 mol%: 90 mol%, 20 mol%: 80 mol%, 30 mol%: 70 mol%, 100 mol%: 0 mol%.

2.2. Optical Measurements

Absorption spectra were measured using an ultraviolet/visible/near-infrared spectrophotometer (V-670 UV/Vis/NIR Spectrophotometer (JASCO)). Emission spectra were measured using a spectrophotometer (FP-6500, (JASCO)).

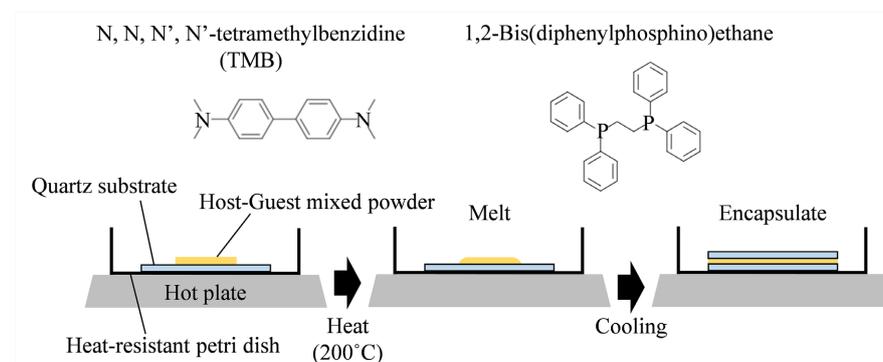


Figure 1. Schematic diagram of organic phosphorescent crystal fabrication.

2.3. Powder-XRD Measurements

The powder XRD measurements of the fabricated OLPL crystals were performed on a RINT-2200 X-Ray Diffractometer (Rigaku, CuK α , 40 kV, 20 mA, 2°/min, $2\theta = 2^\circ - 40^\circ$).

3. Results and Discussion

Table 1 shows the results of irradiating the prepared OLPL crystal films with excitation light. Although no luminescence was observed in the Host molecule alone, luminescence was observed in the OLPL crystals prepared with Guest: Host = 1 mol%: 99 mol%, 10 mol%: 90 mol%, 20 mol%: 80 mol%, 30 mol%: 70 mol%. Only in the OLPL crystal films prepared at Guest: Host = 10 mol%: 90 mol%, 20 mol%: 80 mol%, 30 mol%: 70 mol%, green LPL was observed after excitation light irradiation. The OLPL crystal films prepared at Guest: Host = 20 mol%: 80 mol%, showed the longest LPL of about 1.5 s (**Figure 2**).

Figure 3 shows the absorption spectra and emission spectra of the Guest and Host molecular films and Guest-Host mixture films. In the absorption spectra of the guest molecule TMB film, absorption peaks were observed at 250 nm and 400 nm. The peak at 250 nm is the absorption of the benzene ring and the peak at 400 nm is the absorption of the dimethylamino group. Absorption at 400 nm was observed in all OLPL films mixed with guest molecules. In the OLPL film, the absorption peak at 400 nm was observed in two halves. This is due to the fact that there are two dimethylamino groups in the TMB. The absorption peak of the film prepared at Guest: Host = 20 mol%: 80 mol% was closest to that of the TMB film. This indicates that the two dimethylamino groups caused the strongest CH- π interaction at Guest: Host = 20 mol%: 80 mol%. In emission spectra, no fluorescence peaks were observed in the Host molecule alone, but peaks at 400 and 530 nm were observed in all films mixed with the Guest molecule. For mixed with Guest: Host = 1 mol%: 99 mol%, the fluorescence peak intensity at 400 nm was maximum. For mixed with Guest: Host = 20 mol%: 80 mol%, the fluorescence peak intensity at 530 nm was maximum. The fluorescence peak intensities at 530 nm were, in order of intensity, Guest: Host = 20 mol%: 80 mol%, 30 mol%: 70 mol%, 10 mol%: 90 mol%, and 1 mol%: 99 mol%. This order is consistent with the order of magnitude of the absorbance of the peak at 400 nm in the absorption spectra. This suggests that the peak at 530 nm in the emission spectra is the peak of the LPL that is expressed from the interaction caused by the dimethylamino group. In order to elucidate the crystal structure when LPL is observed, XRD measurements of OLPL crystal films prepared with 1,2-Bis(diphenylphosphino)ethane as a host molecule were carried out.

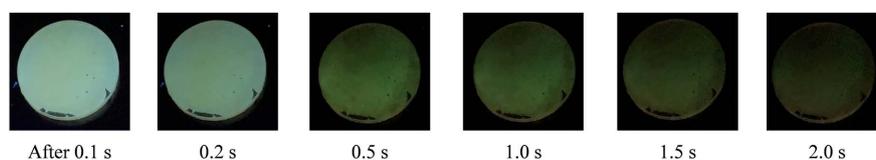


Figure 2. Photographs of LPL from OLPL crystal (20 mol% guest: 80 mol% host).

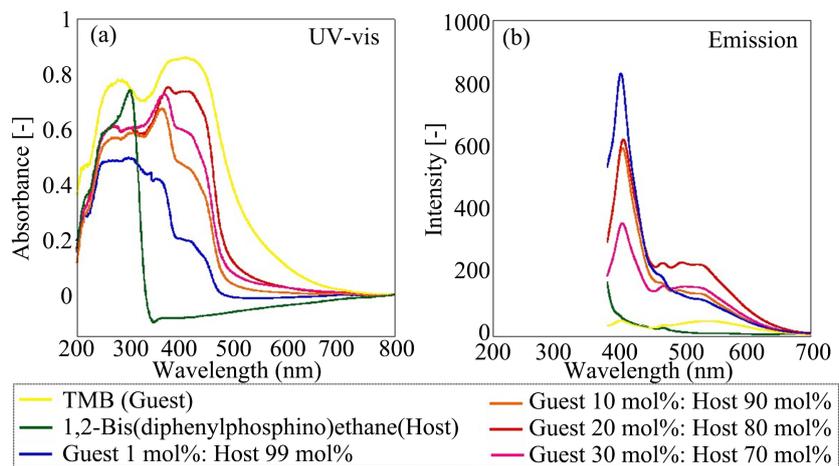


Figure 3. UV-vis spectra (a) and emission spectra (b) of guest, host molecule and guest-host mixed crystal ($\lambda_{ex} = 365$ nm).

Table 1. Luminescence of OLPL crystal.

	Under natural light	Under irradiation of excitation light ($\lambda_{ex} = 365$ nm)
TMB (Guest)		
1,2-Bis(diphenylphosphino)ethane (Host)		
Guest 1 mol%: Host 99 mol%		
Guest 10 mol%: Host 90 mol%		
Guest 20 mol%: Host 80 mol%		
Guest 30 mol%: Host 70 mol%		

Figure 4 shows the results of the measurements. The results for each of the OLPL crystal films were consistent with those of the Host molecule-stable crystals, suggesting that the OLPL crystal films are stable forms of Host. In the peaks with reflections at $(10\bar{1})$, $(20\bar{2})$ and $(30\bar{3})$, a high-angle shift of the peaks was observed with an increase in the ratio of the Guest molecules. The lattice is contracted along the *a*- and *c*-axes, suggesting that the guest molecule is solid-soluted within the crystal structure of the host molecule. **Figure 5** shows the crystal structure of OLPL crystals inferred from the results obtained so far. The Guest molecule, TMB, becomes a substitutional solid solution in the crystal structure of the stable form of the Host molecule (1,2-Bis(diphenylphosphino) ethane) and induces CH- π interactions at four locations. This reduces the energy deactivation of Guest molecules, and LPL is expressed.

The LPL mechanism has been described in previous studies as follows [3]. When the electrons of the host molecule HOMO are excited to LUMO by light absorption, charge transfer occurs from the HOMO of the guest molecule to the HOMO of the host molecule, forming a radical cation of the guest molecule and

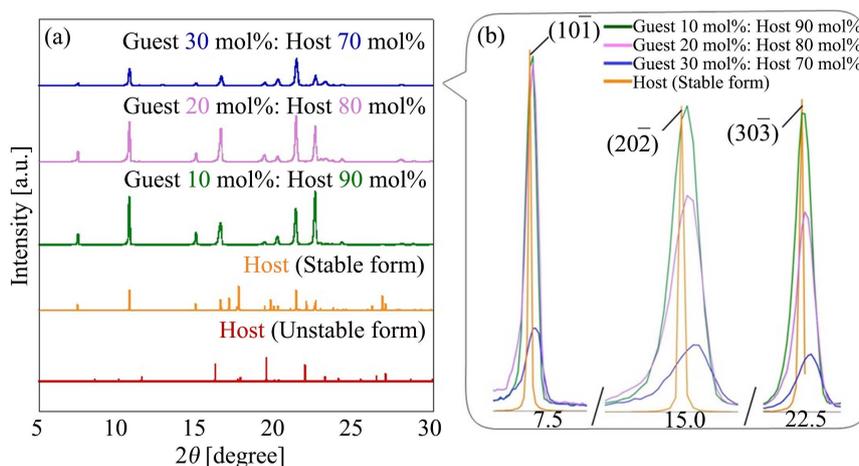


Figure 4. Results of XRD measurements (a) of the OLPL crystals and enlarged view of part.

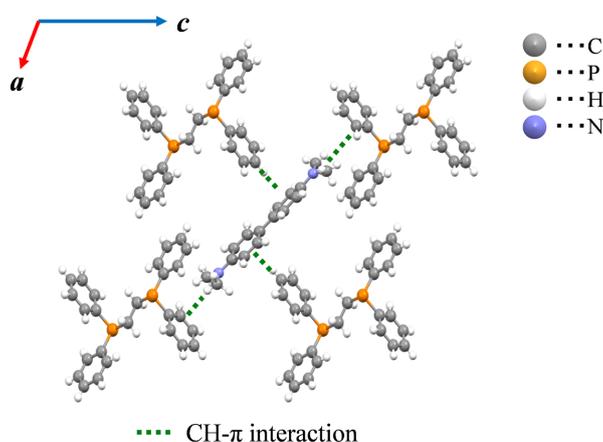


Figure 5. Crystal structure of the speculated OLPL crystal.

a radical anion of the host molecule. The radical anions move on adjacent Host molecules. A charge-separated state is kept. The charge-separated state results in the accumulation of light energy and the expression of LPL. When the light irradiation is stopped, the radical anion stochastically returns to the Guest/Host interface and then returns to the excited state again by charge recombination (transition from the LUMO of the host molecule to the HOMO of the guest molecule). For Guest: Host = 20 mol%: 80 mol% OLPL crystal films, the recombination probability between radical cations and radical anions is reduced and the charge separation state is expected to persist for longer. Conversely, as the Guest molecular ratio increases, the recombination probability between radical cations and radical anions increases, so that the charge-separated state does not persist for a longer period of time and LPL is not likely to develop.

4. Conclusion

LPL was observed in OLPL crystals prepared with TMB as the guest molecule and 1,2-bis(diphenylphosphino)ethane as the host molecule. The longest-lived LPL was observed in the Guest: Host = 20 mol%: 80 mol% film. XRD measurement suggested that the guest molecule is solid-soluted in the crystal structure of the host molecule and that the lattice is contracted in the direction of a- and c-axes. The crystal structure of the OLPL crystal was inferred from the results, and it was inferred that the LPL is triggered by the CH- π interaction. Further research to clarify the design guidelines for OLPL crystals will expand the applications of OLPL crystals and facilitate the development of further long-lived OLPL crystals.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Li, Y., Gecevicius, M. and Qiu, J. (2016) Long Persistent Phosphors—From Fundamentals to Applications. *Chemical Society Reviews*, **45**, 2090-2136. <https://doi.org/10.1039/C5CS00582E>
- [2] Matsuzawa, T., Aoki, Y., Takeuchi, N. and Murayama, Y. (1996) A New Long Phosphorescent Phosphor with High Brightness, SrAl₂O₄: Eu²⁺, Dy³⁺. *Journal of the Electrochemical Society*, **143**, 2670-2673. <https://doi.org/10.1149/1.1837067>
- [3] Hirata, S. (2017) Recent Advances in Materials with Room-Temperature Phosphorescence: Photophysics for Triplet Exciton Stabilization. *Advanced Optical Materials*, **5**, Article 1700116. <https://doi.org/10.1002/adom.201700116>
- [4] Ogoshi, T., Tsuchida, H., Kakuta, T., Yamagishi, T.-A., Taema, A., Ono, T., Sugimoto, M. and Mizuno, M. (2018) Ultralong Room-Temperature Phosphorescence from Amorphous Polymer Poly (Styrene Sulfonic Acid) in Air in the Dry Solid State. *Advanced Functional Materials*, **28**, Article 1707369. <https://doi.org/10.1002/adfm.201707369>
- [5] Al-Attar, H.A. and Monkman, A.P. (2012) Room-Temperature Phosphorescence

- from Films of Isolated Water-Soluble Conjugated Polymers in Hydrogen-Bonded Matrices. *Advanced Functional Materials*, **22**, 3824-3832. <https://doi.org/10.1002/adfm.201200814>
- [6] Ohkita, H., Sakai, W., Tsuchida, A. and Yamamoto, M. (1997) Charge Recombination Luminescence via the Photoionization of a Dopant Chromophore in Polymer Solids. *Macromolecules*, **30**, 5376-5383. <https://doi.org/10.1021/ma970585q>
- [7] Deotare, P.B., Chang, W., Hontz, E. and Congreve, D. (2015) Nanoscale Transport of Charge-Transfer States in Organic Donor-Acceptor Blends. *Nature Materials*, **14**, 1130-1134. <https://doi.org/10.1038/nmat4424>
- [8] Gélinas, S., Van Der Poll, T.S., Bazan, G.C. and Friend, R.H. (2014) Ultrafast Long-Range Charge Separation in Organic Semiconductor Photovoltaic Diodes. *Science*, **343**, 512-517. <https://doi.org/10.1126/science.1246249>
- [9] Jailaubekov, A.E., Willard, A.P., Tritsch, J.R., Chan, W.L., Sai, N., Gearba, R., *et al.* (2013) Hot Charge-Transfer Excitons Set the Time Limit for Charge Separation at Donor/Acceptor Interfaces in Organic Photovoltaics. *Nature Materials*, **12**, 66-73. <https://doi.org/10.1038/nmat3500>
- [10] Doki, N. and Yokota, M. (2015) Luminescent Characteristic of Organic Compound-Containing Inorganic Crystal at Room Temperature. *Advances in Chemical Engineering and Science*, **5**, 441-446. <https://doi.org/10.4236/aces.2015.54045>
- [11] Doki, N. and Yokota, M. (2021) Pyrene Nanocrystals Crystallized by a Continuous Flow Microreactor. *Journal of Materials Science and Chemical Engineering*, **9**, 1-6. <https://doi.org/10.4236/msce.2021.911001>