

Optical study on the morphology of organic molecules in thin solid films

Taiju Tsuboi

Faculty of Engineering, Kyoto Sangyo University, Kamigamo, Kyoto, Japan

Phone:+81-75-705-1899, E-mail: tsuboi@cc.kyoto-su.ac.jp

Abstract

Unlike the case of Ir(ppy)_3 , various aggregates of PtOEP including dimer are formed in PtOEP-doped films and neat film. Such a difference is due to difference of competition among solid state solvation effect, dipole-dipole interactions between dopant molecules, and intermolecular covalent bonding.

1. Introduction

Thin film layers in organic light emitting diodes (OLEDs) are formed by thermal evaporation in vacuum or spin-coating. The electroluminescence (EL) characteristics of multilayer OLEDs have been explained using the properties of individual, isolated organic molecules in the emitting layer although each molecule has interaction with not only neighboring molecules within the same layer but also molecules of neighboring layers. It is not confirmed that each molecule is present completely independently from neighboring molecules without formation of any aggregate or polycrystal.

The distribution and geometry of organic molecules in the layers determine the electrical and optical properties of OLEDs because they change the structure and alignment of the electronic energy levels of the constituent molecules. Therefore it is necessary to investigate the morphology of thin amorphous films. No detailed analysis, however, has been made on the morphology of organic thin films except films of tris(8-hydroxyquinoline) aluminum (Alq_3) doped in N,N' -bis(3-methylphenyl)- N,N' -bis(phenyl)-benzidine (TPD) and of [2-methyl-6-[2-(2,3,6,7-tetrahydro-1H, 5H-benzo [ij]quinolizin-9-yl) ethenyl]-4H-pyran-4-ylidene] propane-dinitrile (DCM2) [1].

It is suggested that the polar Alq_3 and DCM2 molecules form ordered domains consisting of many Alq_3 and DCM2 molecules, respectively [1]. It, however, is not clear whether the model of domain formation is applicable to the other organic molecules. We study the morphology of organic thin films (TPD, CBP, Ir(ppy)_3 , PtOEP, mCP, etc) from the photoluminescence (PL), excitation, EL and absorption spectra at not only room temperature but

also low temperature like 10 K. Especially we investigate whether each molecule is distributed randomly without strong interaction between the neighboring molecules or several molecules form aggregates such as dimer and trimer.

2. Results

2.1 TPD and Ir(ppy)_3

Figure 1 shows the temperature dependence of PL spectra of a TPD film doped with 5wt% fac tris(2-phenylpyridine) iridium [Ir(ppy)_3] [2]. The dopant Ir(ppy)_3 shows almost the same PL line shape between 290 and 10 K except a relatively highly resolved vibronic structure at low temperature.

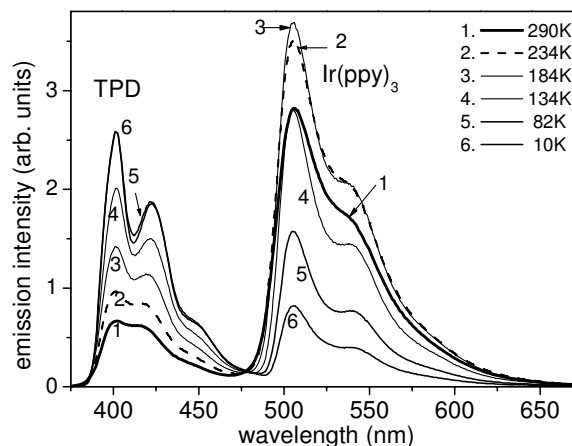


Figure 1 Photoluminescence spectra of a film of TPD doped with 5wt% Ir(ppy)_3 at various temperatures, which was excited at 360 nm.

On the other hand, TPD host shows different line shape between 290 and 10 K, e.g. the peak height ratio of the 0-0 line (i.e. zero phonon line due to transition from the vibrational quantum number $m=0$ in the excited state to the vibrational quantum number $n=0$ in the ground state) at 404 nm to the vibronic 0-1

line at 417 nm decreases considerably with increasing temperature from 10 K to 290 K. At 290 K, the 0-1 line peak height is nearly the same as the 0-0 line height. Such an unusual decrease of the 0-0 line peak height is also observed in neat film of TPD.

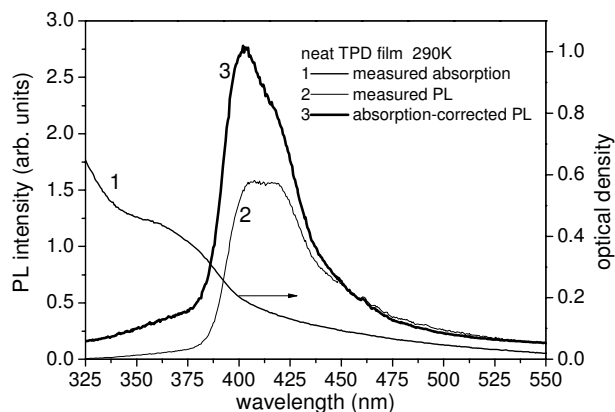


Figure 2 Absorption spectrum of neat TPD film at 290 K (curve 1), and the observed and corrected emission spectra of TPD which are obtained from the same film at 290 K (curves 2 and 3, respectively) Curve 3 was derived after correction of self-absorption.

The absorption band of TPD shifts to low energy with increasing temperature, and its low energy tail overlaps strongly with the emission band. We corrected the emission spectra taking into account the self-absorption, and obtained that the corrected 0-0 lines becomes higher at high temperatures than the 0-1 line as observed at low temperatures as shown in Fig. 2. From comparison of the corrected emission spectra with the observed spectra, it is concluded that the unusual decrease of the 0-0 line at high temperatures such as 290 K is due to the self-absorption.

Quite similar temperature dependence of emission spectra is observed in neat film of Ir(ppy)₃ (see Fig. 3). For example, unlike the case of Ir(ppy)₃ doped as the dopant (Fig. 1), much larger peak height decrease of the 0-0 emission line than the 0-1 line is observed at high temperatures in addition to strong overlap of the low energy tail with the 0-0 line. The unusual decrease of the 0-0 line is also due to the self-absorption. Besides the emission band due to

monomer, any emission band due to aggregates such as dimer and trimer was not observed in TPD and Ir(ppy)₃ neat films.

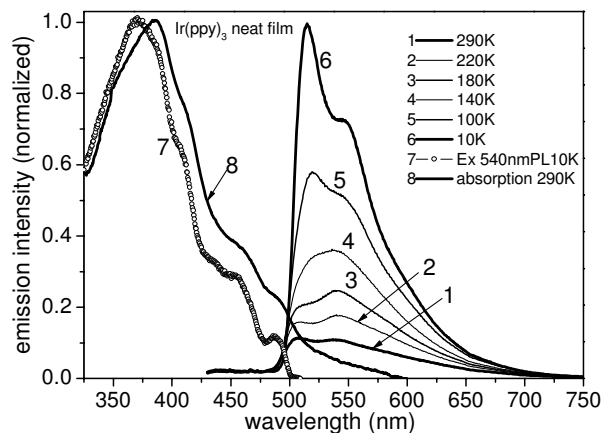


Figure 3 Photoluminescence spectra of Ir(ppy)₃ neat film at various temperatures (curves 1-6), which was excited at 360 nm, together with excitation (Ex) spectrum for 540 nm emission at 10 K (7) and absorption spectrum of the neat film at 290 K (8).

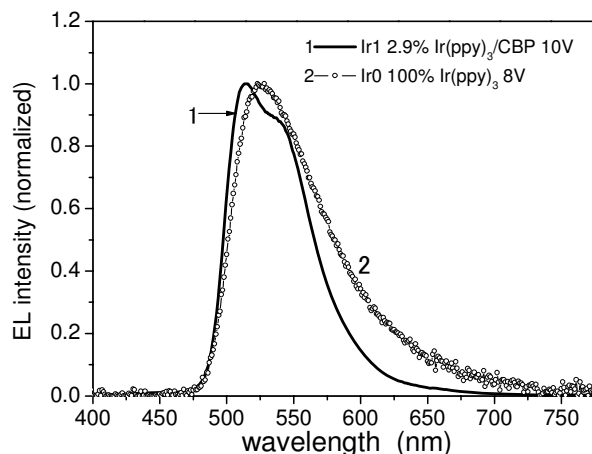


Figure 4 Electroluminescence spectra of multilayer structure OLED (Ir1) and monolayer OLED (Ir0).

Figure 4 shows the EL spectra of multilayer OLED with emitting layer of 2.9wt% Ir(ppy)₃-doped CBP (named Ir1) and of monolayer OLED with layer of 100% Ir(ppy)₃ (Ir0). The device structures are

Ir1:
ITO/ α -NPD/2.9wt%Ir(ppy)₃:CBP/BCP/Alq₃/LiF/Al,
Ir0 :
ITO/100%Ir(ppy)₃/LiF/Al.

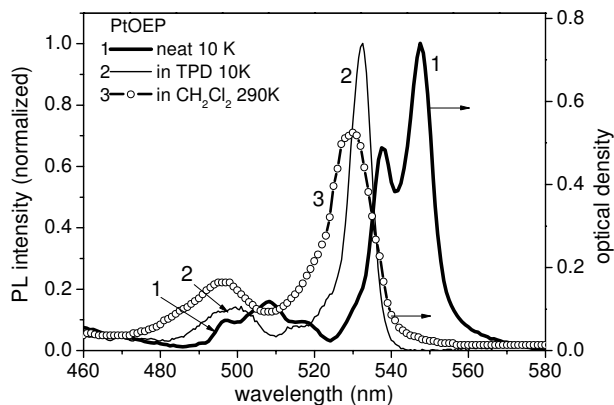


Figure 5 Absorption spectrum of neat PtOEP film at 13 K (curve 1) and excitation spectrum for 640 nm emission of PtOEP in a film of TPD doped with 2 wt% PtOEP at 10 K (2), together with the absorption spectrum of PtOEP in CH₂Cl₂ solvent at 290 K (3).

The Ir1 OLED has an EL band peak at 513 nm, while the Ir0 at 524 nm. The peak shift of Ir0 is due to self-absorption because of much more intense absorption due to Ir(ppy)₃ in Ir0 than in Ir1. No additional EL band is observed besides monomer emission band in Ir0. This is consistent with the PL spectra of Ir(ppy)₃ neat film. It is confirmed that Ir(ppy)₃ does not form aggregate even in neat film.

2.2 PtOEP

Figure 5 shows the absorption spectrum of neat film of platinum octaethyl porphyrin (PtOEP) at 13 K and the excitation spectrum of film of TPD doped with 2 wt% PtOEP at 10 K, together with the absorption spectrum of diluted PtOEP in CH₂Cl₂ solution. The spectrum of doped film is the same as that of PtOEP in the solution except peak shift due to the solvation effect. Additional absorption bands appear at 538 and 547.5 nm at the low energy side of the band at 532.5 nm due to PtOEP monomer in neat film, which are attributed to the dimer and trimer, respectively.

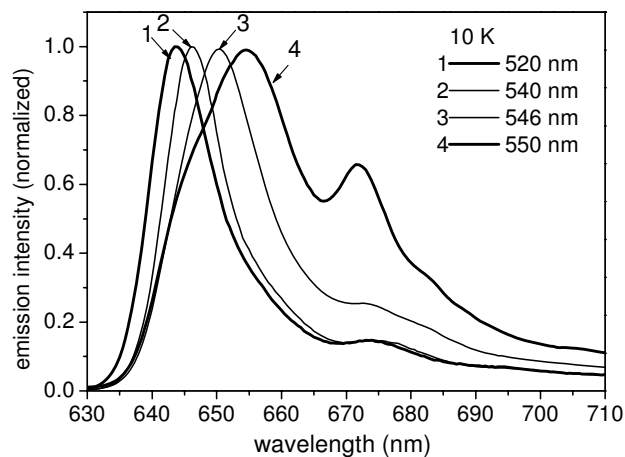


Figure 6 Photoluminescence spectra of PtOEP in a film of TPD doped with 5wt% PtOEP, excited with lights of various wavelengths at 10 K

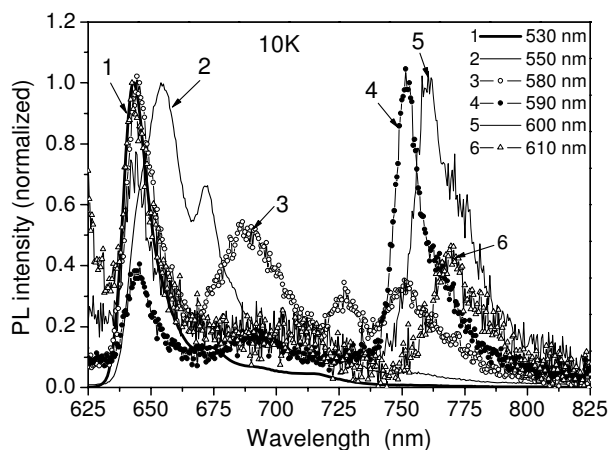


Figure 7 Photoluminescence spectra of PtOEP in film of TPD doped with 5wt% PtOEP at 10 K, which was excited with lights of various wavelengths.

Coexistence of monomer with aggregates such as dimer and trimer is confirmed by emission spectra of Fig. 6 which were obtained by excitation into the various absorption bands. Each of monomer, dimer and trimer gives different emission bands. The intense emission band exhibits red shift on going from monomer to dimer to trimer.

When the film of 5wt% PtOEP doped in TPD is excited with lights of wavelengths longer than 550 nm at 10 K, additional emission bands are observed at 750-800 nm as shown in Fig. 7. The main emission bands have peaks at 688, 751, 760 and 770 nm. The appearance of these emission bands depends on the excitation wavelength. These emission bands are attributed to large aggregate, which consists of many PtOEP molecules, because these emission bands are also observed in PtOEP neat films. Figure 7 indicates that such aggregates are present in not only the 100 % neat film but also a lightly doped film like 5 wt % concentration.

Figure 8 shows the EL spectra of various OLEDs based on PtOEP, named Pt3, Pt2, Pt5 and Pt0. The Pt3 and Pt2 multilayer OLEDs have emitting layer of CBP doped with 5 and 7 wt% PtOEP, respectively, while the Pt5 and Pt0 OLEDs have emitting layer of 100 % PtOEP films. The device structures are

Pt2:

ITO/ α -NPD/7wt%PtOEP:CBP/BAIq/Alq₃/LiF/Al,

Pt3:

ITO/ α -NPD/5wt%PtOEP: CBP/BAIq/Alq₃/LiF/Al,

Pt5:

ITO/ α -NPD/100% PtOEP/BAIq/Alq₃/LiF/Al,

Pt0 :

ITO/100%PtOEP/LiF/Al.

The peak position of EL due to PtOEP is different among the four OLEDs, i.e. at 647, 648, 652 and 658 nm for Pt3, Pt2, Pt5 and Pt0, respectively. The 647, 652 and 658 nm peaks are attributed to monomer, dimer and trimer, respectively. Red shift is observed with increasing the PtOEP concentration. In the case of Pt0, the peak shifts to low energy with increasing applied voltage, e.g. 654.5 nm at 10 V, while 658 nm at 17 V. In addition to the EL due to monomer, the PtOEP neat films give EL bands due to aggregates including EL band at 688 nm which is observed in PL (see curves 3 and 4 of Fig. 8).

The Pt5 OLED shows different EL spectrum from the Pt0 OLED although these OLEDs contain the same 100% PtOEP film. This indicates that the dimer and trimer with different concentration ratios are formed in the two OLEDs. Therefore it is suggested that the conformation depends on the structure of device because of interaction with molecules in neighboring layers. It is noted that the aggregate with the lowest T₁ state (e.g. trimer of the three conformations) gives the

highest EL peak in OLED. This is caused by higher concentrations of dimer and trimer than monomer in addition to energy transfers from monomer to dimer and to trimer.

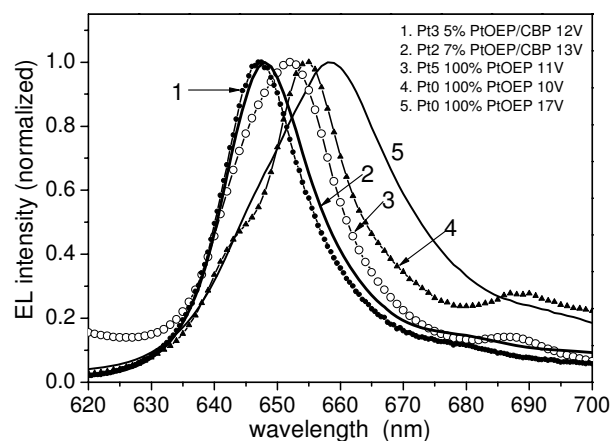


Figure 8 Electroluminescence spectra of OLEDs based on PtOEP. Curves 1, 2, 3, 4 and 5 are obtained from Pt3, Pt2, Pt5, Pt0 and Pt0 OLEDs under applied voltages of 12, 13, 11, 10 and 17 V, respectively.

2.3. mCP

Figure 9 shows the PL and excitation spectra of 1,3-bis (9-carbazolyl) benzene (mCP) in three films of polystyrene doped with 1, 5 and 20 wt% mCP and in mCP neat film at 10 K [3]. The 0-0 line peak position of the PL spectrum shows red shift due to self-absorption, and the amount of shift becomes large with increasing the dopant concentration from 1 to 5 to 20 wt%. No change is observed for the 0-1 line peak position between the 1 and 5 wt% mCP films, but the 0-1 line of 20 wt% film shows red shift, i.e. peak at about 365 nm in 20 wt% film, while at 360 nm in 1 wt% film. This shift is understood by solid state solvation effect [4] which is more strong in highly doped film than in lightly doped films. This is confirmed from peak position of the corresponding 0-0 absorption line which is monitored by the excitation spectra of curves 1', 2' and 3' of Fig. 9.

In the neat film, sharp emission lines are observed at 347.5 nm (called a0 line, hereafter, see Fig. 8), 351.9 nm (b0), 355 nm (c0), 364.2 nm (a1), 368.6 nm (b1),

373.4 nm (c1), 382.8 nm (a2), 387.5 nm (b2) and 392 nm (c2). The excitation spectrum of the neat film has additional bands at the longer wavelength side in each of the absorption bands due to monomer, which are observed in lightly doped 1 wt% film, for example, at 342 and 347 nm (called B and C lines, respectively).

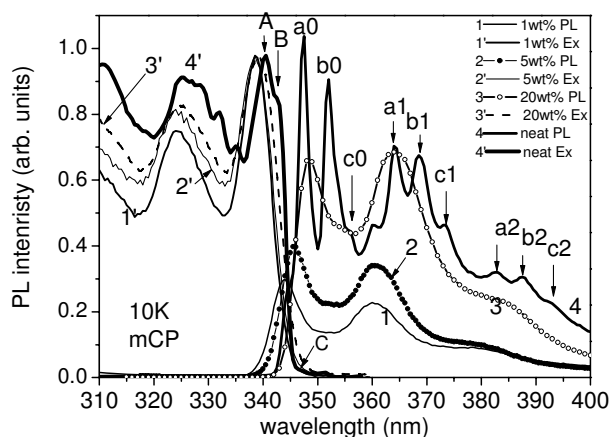


Figure 9 Photoluminescence (PL) and excitation (Ex) spectra of mCP in films of polystyrene doped with 1, 5 and 20 wt% mCP (curves 1(1'), 2(2') and 3(3'), respectively) and in mCP neat film (curve 4 (4')) at 10 K. The PL and Ex spectra were obtained by 305 nm excitation and for 375 nm emission, respectively.

From characteristics of the emission peaks with vibronic progression and from comparison with lightly doped films, it is suggested that there are at least three kinds of conformations in the neat film. One is monomer responsible for the a0, a1 and a2 emission lines and the A absorption line at 340.6 nm, another is dimer responsible for the b0, b1 and b2 emission lines and the B absorption line, and the other is trimer responsible for the c0, c1 and c2 emission lines and the C absorption line. The a0, a1 and a2 emission lines are attributable to the 0-0, 0-1 and 0-2 vibrational lines associated with the singlet state S_1 of monomer, respectively, the b0, b1 and b2 emission lines are attributable to the 0-0, 0-1 and 0-2 lines associated with the S_1 state of dimer, and the c0, c1

and c2 emission lines are attributable to the 0-0, 0-1 and 0-2 lines associated with the S_1 state of trimer.

3. Conclusion

Molecules confined in thin film take their stable positions and form conformation finally after they are randomly distributed by evaporation or spin-coating. When the concentration of dopant is high and the intermolecular distance becomes short, molecules are possible to form aggregates by intermolecular covalent bonding. The PL, EL and absorption spectra certainly indicate that PtOEP molecules form not only small aggregate such as dimer but also large aggregate in neat film. Dimer of PtOEP was formed even in lightly PtOEP-doped TPD, polystyrene and polycarbonate films. Dimer and trimer are also formed in mCP neat film. On the other hand, neither dimer nor aggregate is found in $\text{Ir}(\text{ppy})_3$ neat film and heavily $\text{Ir}(\text{ppy})_3$ -doped films. Alq_3 shows peak shift in the emission bands with increasing concentration of the dopant Alq_3 [1], which is due to the solid state solvation effect. We tried to find dimer and aggregate of Alq_3 in neat film at low temperatures like 10 K, but we could not observe them.

It is suggested that there are two groups in the doped and neat films. The first group is that the constituent molecules form aggregates as the cases of PtOEP and mCP, the second group is that the constituent molecules do not form any aggregate as the cases of Alq_3 and $\text{Ir}(\text{ppy})_3$.

Formation of aggregate is due to the intermolecular covalent bonding. Square planar structure PtOEP has plane of porphyrin which has a strong tendency towards π - π stacking. Therefore dimer is easily formed, while monomer PtOEP also exists together with the aggregates even in heavily doped films. Alq_3 and $\text{Ir}(\text{ppy})_3$ molecules do not have such a planar structure, resulting in poor stacking. The time dependent density function theory calculation for Alq_3 shows absence of effective HOMO overlaps between neighboring molecules [5]. This indicates that formation of stable dimer and trimer is difficult in Alq_3 film although each of Alq_3 molecules has dipole-dipole interaction with neighboring molecules.

In conclusion, the molecular conformations in thin films are determined by the competition and balance among solid state solvation effect, dipole-dipole interactions between guest molecules, and intermolecular covalent bonding, which is strongly depending on the molecular geometrical structure.

4. Acknowledgements

We thank Profs. Alfons Penzkofer and Chin-Ti Chen for kindly providing organic thin films and Mr. Hideyuki Murayama for assisting the optical measurements. This work was partially supported by the Grant-in-Aid for the Scientific Research from the Japan Society for Science Promotion.

References

- [1] M.A. Baldo, Z.G. Soos, S.R. Forrest, Chem. Phys. Lett. **347**, 297 (2001).
- [2] T. Tsuboi, H. Murayama, A. Penzkofer, Thin Solid Films **499**, 306 (2006).
- [3] M.F. Wu, S.J. Yeh, C.T. Chen, H. Murayama, T. Tsuboi, W.S. Li, I. Chao, S.W. Liu, J.K. Wang, to be published.
- [4] C.F. Madigan, V. Bulovic, Phys. Rev. Lett. **91**, 247403 (2003).
- [5] B.C. Lin, C.P. Cheng, Z.Q. You, C.P. Hsu, J. Am. Chem. Soc. **127**, 66 (2005).