Formation dynamics of small molecular/polymer hybrid organic semiconductor thin films for light emitting diodes

H. Kon[1], Y. Tsuji [1, 2] *, C. Kurosawa [1], and Y. Yamaguchi [1]

1 Department of Chemical System Engineering, The University of Tokyo

2 Environmental Science Center, The University of Tokyo

Email of corresponding author: tsuji@esc.u-tokyo.ac.jp

Presented at the 17th International Coating Science and Technology Symposium

September 7-10, 2014, San Diego, CA, USA

Introduction

In recent years, much efforts has been paid to the study of the organic light-emitting diodes (OLEDs) based on small molecule and polymers for practical applications in lighting devices and flat-panel displays[1]. Between small molecular thin films and polymers, there is a clear difference in the method used for fabricating the devices: vapor phase deposition for small molecules and solution process for polymers. Small molecules can be synthesized and purified more easily than polymers, but their vapor deposition process increases the fabrication cost of the devices and it is difficult to be larger scale devices. So today small molecule OLEDs fabricated by solution process are attracting research interests. Several groups have reported small molecule OLEDs fabricated by solution process using well designed and synthesized small molecules[2-3], such as Iridium complexes and aluminum chelates. The use of phosphorescent materials, such as iridium complexes, as their emitting materials shows much higher efficiencies than OLEDs that use conventional fluorescent emitting materials[4-6].

We focus on the phosphorescent organic small molecular thin films using host-guest system fabricated by solution process. We have already found that PL intensity decreases when guest molecule forms domains, due to the declination of the efficiency of energy transfer from host molecule to guest molecule. In this study, we added polystyrene with different molecular weight to small molecule organic materials for emission layer expecting the resolution of forming domains of guest molecule. We also investigate the formation mechanism of organic thin films from solutions during drying by using in-situ measurements. We discuss the effect of polystyrene addition on nanostructure and optical properties of thin films considering film formation dynamics.

Experimental Methods

We used 4,4-bis(9carbazolyl)-2,2-dimethylbiphenyl (Fig.1 (a)) as host material and Tris(2phenylpyridinate)iridium(Ⅲ) deribvative (Fig.1 (b)) as guest material, and polystyrene 0-3 (each molecular weight: PS0-30,000 PS1-900,000 PS2-440,000 PS3-1,800,000) in this study. We prepared host-guest solution and polystyrene solution separately; host material and guest material were dissolved in toluene (total amount of solute is 1wt. %) and stirred for 3min at ambient temperature, polystyrene was also dissolved in toluene (1wt. %) and stirred 30min at 90℃. We mixed these two solution and stirred for 3min at ambient temperature. This solution was spin-coated on silicon substrate at 1000 rpm for 60s. During spinning, we observed light scattering by irradiating the surface of the droplet with a semiconductor laser (670 nm) and PL spectra by irradiating with a condensing deuterium lamp (300 nm). The static optical properties were determined by UV-vis absorption and PL intensity measurement.

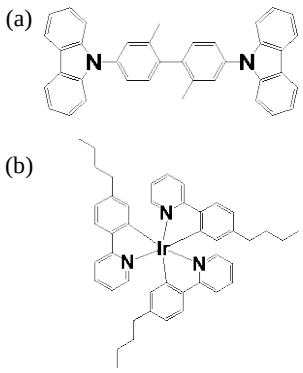

Fig.1. The structure of (a) host material, (b) guest material used in this study.

Results and Discussion

Optical Properties

The absorption peak position was 300 nm for all films in this study. We standardized absorption intensity by host molecular weight, and found that adding polystyrene to small molecule increased the absorption intensity. The increase of polystyrene concentration showed higher absorption (Fig.2).

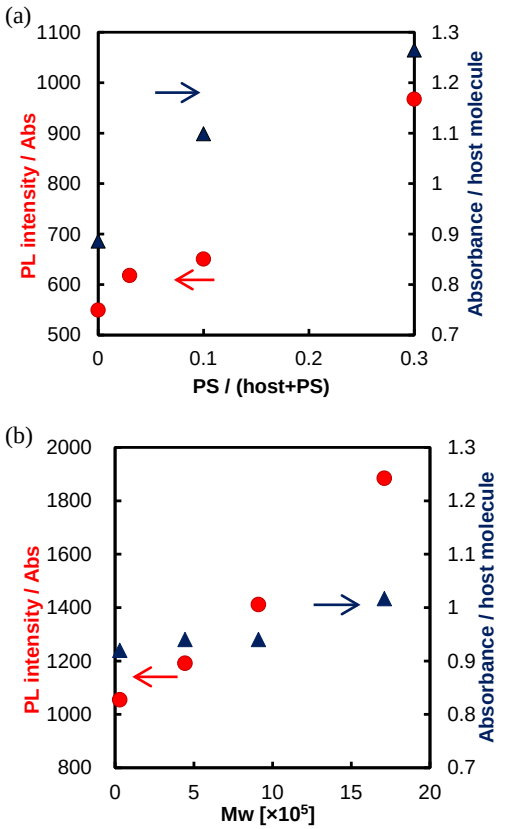

Fig.2. Optical properties of thin films depending on (a) PS concentration, (b) molecular weight of PS.

Similarly, PL peak position was 610 nm for all films. We standardized PL intensity by absorption, and defined “light-emitting efficiency”, to exclude the effect of absorption. It was found that “light-emitting efficiency” increased in proportion to molecular weight and additive amount of polystyrene (Fig.2). This result shows adding polystyrene gives better optical properties.

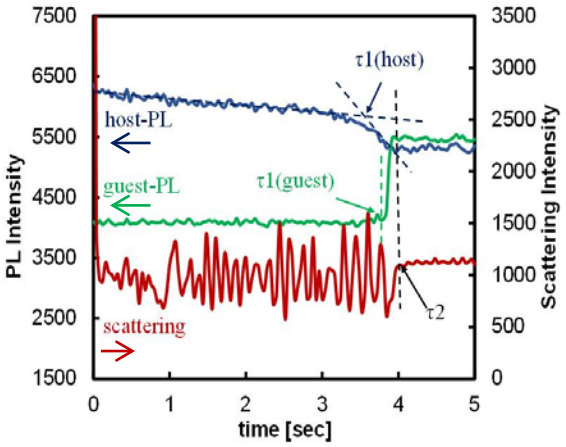

Fig.3. The typical spectrum of observation light scattering and PL during spinning

Dynamics of Film Formation

The typical spectrum of observing light scattering and PL shows in Fig.3. The host-PL, gradually decreased, and inflection point of decreasing intensity was observed at 3.38s, this point we defined τ1(host). Initial decrease is caused by concentration quenching, secondry decrease is caused by starting energy transfer host molecule to guest molecule. Finally PL intensity became constant. Guest-PL intensity showed constant value, increased sharply, and finally became constant. We defined this increasing point τ1(guest). Fluctuation of scattering intensity was stopped and the PL intensity of host and guest became constant value, we defined τ2, indicating that the film formation was completed at τ2.

Then, we investigated the effect of adding polysryrene to small molecule from the aspect of dynamics. Adding polystyrene delayed the emitting onset time of guest molecule (τ1(guest)) (Fig.4). Additionaly, τ1(guest) increased in proportion to molecular weight and additive amount of polystyrene. While τ1(host) was

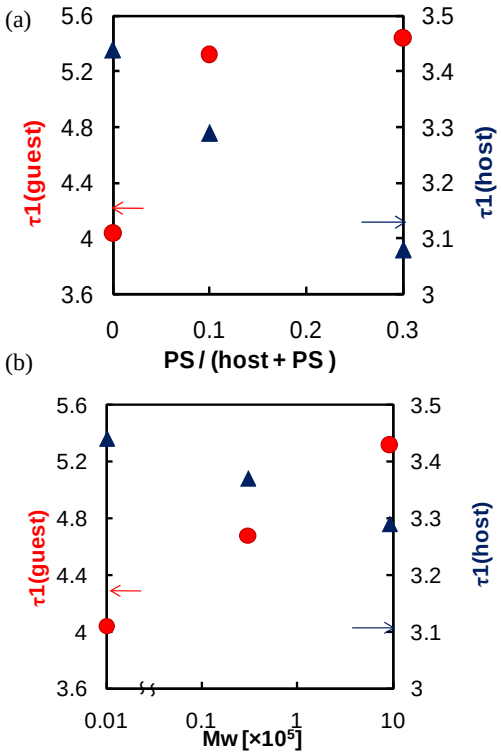

Fig.4. τ1(guest) and τ1(host) depending on (a) additive amount of PS, (b) molecular weight of PS.

decreased by adding polystyrene due to the increase of density. Then, we calculated the drying rate and the concentration of the solute at τ1(guest). Adding polystyrene decreased drying rate and enhanced concentration at τ1(guest). It was suggested that nucleation of guest molecule started at higher concentration, therefore the frequency of nucleation became higher, and the size of guest domain became more smaller. So, adding polystyrene enlarged the amount of interfacial surface area between host molecule and guest molecule, and enhanced “light-emitting efficiency”.

Conclusion

Adding polystyrene to small molecule showed higher absorption intensity by host molecular weight and “light-emitting efficiency”, and it increased in proportion to molecular weight and additive amount of polystyrene. Adding polystyrene enhanced the static optical property due to the increasing of the amount of surface area between host molecule and guest molecule.

Reference

[1] *L. Akcelrud, Prog. Polym. Sci. 28 (2003) 875.*

[2] *S. Penna, A. Reale, R. Pizzoferrato, G.M.T. Beleffi, D. Musella, W.P. Gillin, Appl. Phys. Lett. 91 (2007) 021106.*

[3] *L.D. Hou, L. Duan, J. Qiao, W. Li, D.Q. Zhang, Y. Qiu, Appl. Phys. Lett. 92 (2008) 263301.*

[4] *Marijn Goes, Jan W.Verhoeven, Hans Hofraat, and Klemens Brunner, CHEMPHYSCHEM 4, (2003) 349-358.*

[5] *N.Rehmann, D.Hertel, and K.Meerholz, Appl. Phys. Lett. 91 (2007) 103507*.

[6] *Lin He, Junfeng Liu,..et al, Thin Solid Films 518 (2010) 3886–3890.*