THE FÖRSTER-TYPE EXCITON QUENCHING MECHANISM AND ITS IMPACT TO THE QUANTUM EFFICIENCY AND EXCITON DIFFUSION IN ORGANIC SEMICONDUCTOR

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Abstract

Organic light-emitting diodes (OLEDs) have emerged as one of the most important generallighting technologies of the future. The current state-of-the-art OLED utilizes various differentlayers which function separately as carriers transport, carriers and excitons blocker, and emittinglayer. The emission layer of the OLED is normally formed by a host-guest system obtained byco-evaporating a small amount of guest molecule in the matrix of host material. It is generallyaccepted that in a host-guest system, concentration quenching is caused by molecules aggregation.As concentration of guest molecule increases, a drop in quantum efficiency is followed by a redshiftin the emission spectrum, characteristics of aggregate state. Here we show that concentrationquenching is also caused by another Förster-type interaction. We investigate this Förster-typeexciton quenching process in various organic molecules and its effect to the exciton diffusion.

1. Introduction

a. *Organic Semiconductor*

Organic semiconductor is a class of organic material which has an alternating single and double carbon-carbon covalent bonds, or simply called conjugated bonds.[1] Conjugated bonds require the electrons in the carbon atoms to form sp_2 hybrid orbital (σ-bond) which lets an electron to form a loose p_z-orbital which is perpendicular to the plane containing all the carbon atoms. The delocalized π-electrons are free to move within the molecule and enable charge transport in organic materials. In analogy to the inorganic semiconductor, organic semiconductor also possesses a valence band-like orbital which is called the highest occupied molecular orbital (HOMO) and a conduction band-like orbital which is called the lowest unoccupied molecular orbital (LUMO). The bandgap is formed by the HOMO and LUMO levels.

b. *Organic Light Emitting Diode*

Figure 1 shows a diagram of the various processes in OLED. Prior the light emission, quasi-particle, excitons, were formed by recombination of electrons and holes injected from the respective electrodes. In the process of carrier recombination, not all electrons or holes contribute to the excitons formation responsible to efficiency losses. This is due to the imbalance of carrier injections and transportations ($\Box_{e-h}$) in the device. Preceding the exciton formations, only one quarter (singlet) of those excitons can recombine radiatively by fluorescence, while the rest (triplet) decay through non-radiative channels due to the spin disparity. Some fraction of the singlet exitons will also decay non-radiatively. To harvest the triplet excitons, phosphorescent dopant (host-guest system) was introduced.[2] Phosphorescent molecule mixes the singlet and triplet excitons by spin-orbit coupling utilizing a heavy metal ligand. In planar structure like OLED, almost 80% or so of the light produced in the organic semiconductor is absorbed by the cathode-organic surface plasmon mode and waveguide.
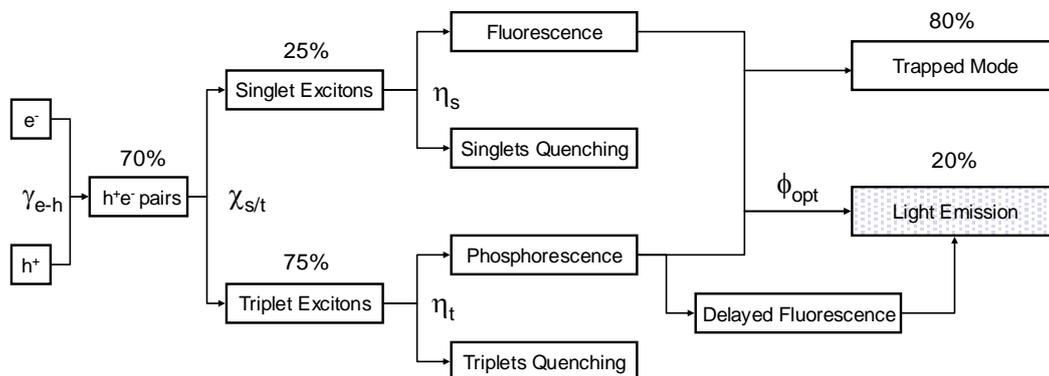
Figure 1 Electroluminescence diagram in OLED

c. *Host-Guest System in OLED*

The emission layer of OLED normally consists of a host-guest system formed by co-evaporating a small amount of guest molecule in the matrix of host material. Most excitons are formed in the matrix host which then transfers the energy to the guest molecule where final emission takes place. Host-guest system minimizes aggregation of guest molecules so as to enable high quantum yield. It is generally accepted that in a host-guest system, concentration quenching occurs because of molecule aggregation. As concentration of guest molecule increases, a drop in quantum efficiency is followed by a red-shift in the emission spectrum, characteristics of aggregate state. Recently our group has extensively studied other factors that cause excitonic quenching in organic semiconductor. Here we review some of the progress made toward understanding the excitonic concentration quenching and their propound impact to the dynamics of the exciton in the organic semiconductor.

2. Experimental

The OLED was fabricated on ITO glass (50 Ω/square) which was earlier subjected to the standard cleaning procedure that involves ultra-sonication in acetone, ethanol, rinsing in de-ionized water and oxygen plasma treatment at 15 Pa for 3 minutes. Evaporation of organic materials and metals was carried out in a high vacuum condition of about 2×10^{-4} Pa with deposition rates of 0.5-4 Å/s. The quartz crystal microbalance thickness sensor was positioned near the ITO glass for better accuracy. For each run, up to four samples were fabricated simultaneously without breaking the vacuum, to ensure similar deposition condition.

Electroluminescence (EL) spectra of the fabricated devices were measured with a calibrated PR650 Spectra Scan spectrometer. Current density–voltage characteristics were recorded by Yokogawa source measurement unit. We assumed the emission pattern was Lambertian, and calculated the EQE from the luminance, current density and EL spectrum.All measurements were carried out at room temperature under ambient atmosphere without any encapsulation.

For the study of the concentration-quenching in phosphorescent host-guest system we employedN,N'-di(naphth-2-yl)-N,N'-diphenyl-benzidine (NPB) as the hole transporting layer, 4,4'-N,N'-dicarbazole-biphenyl (CBP) as the host, *fac*-tris(2-phenylpyridinato- N,C2')iridium(III) [Ir(ppy)$_3$] as the guest, 2,9-dimethyl-4, 7-diphenylphenanthroline (BCP) as the hole blocking layer, and tris-(8-hydroxyquinoline) aluminum (Alq$_3$) as the electron transporting layer. Since excitons are formed at both NPB/CBP and CBP/BCP interfaces, the guest was evaporated at these interfaces to harvest the excitons.

For the study of the concentration-quenching in fluorescent host-guest system we employed NPB as the hole transporting layer, Alq$_3$ as the host, 4 –(dicyanomethylene) - 2 - methyl- 6 - (*p* - dimethyl aminostyryl)-4H-pyran (DCM) as dopant, andBCP as the hole blocking layer and also the electron transporting layer.

To study the variation of exciton diffusion length as a function of intermolecular spacing, we investigated the exciton diffusion and quenching utilizing a blue OLED with a single exciton source. The blue OLED has a structure of ITO/NPB/BCP/Alq$_3$/Mg:Ag, where ITO is indium-tin-oxide as the anode, NPB is N,N'-di(naphth-2-yl)-N,N'-diphenyl-benzidine as the

hole transporting layer, BCP is 2,9-dimethyl-4, 7-diphenylphenanthroline as the hole blocking layer, Alq$_3$ is tris-(8-hydroxyquinoline) aluminum as the electron transporting layer, and Mg:Ag is a mixture of magnesium and silver (ratio 10:1) as the cathode. Ir(ppy)$_3$ was deposited as the guest molecule in the BCP-host by sequential doping [Ir(ppy)$_3$/BCP multiple-layer].

3. Concentration-quenching in phosphorescent host-guest system

To investigate the mechanisms responsible for concentration quenching in phosphorescent host-guest system, utilizing a specially designed OLED devices with emission layer consisting of a few repeating cells, similar to a multiple quantum well structure.[3] Each cell consists of a sequentially deposited host and guest materials. Figure 2a shows our specially designed multiple quantum well-like structure. Variation of the thickness of the guest layer in each cell enables the study of the effect of molecule aggregation to the quantum efficiency. On the other hand, variation of the thickness of host layer leads to the observation of a new long range quenching mechanism which will be discussed here.
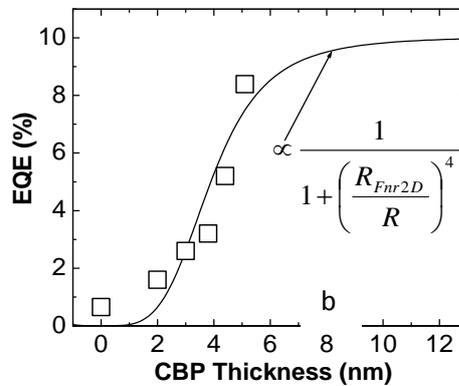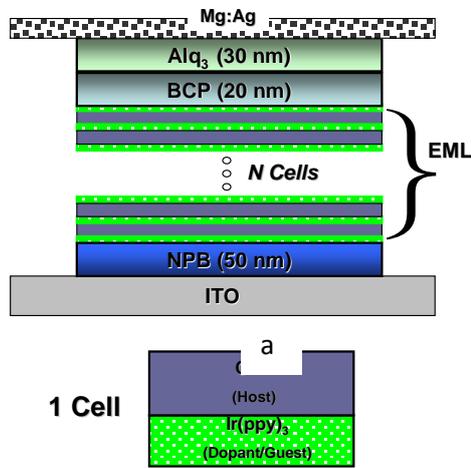
Figure 2 *a) The multiple quantum well-like structure used to investigate the concentration quenching mechanism in OLED. b) The plot of external quantum efficiency (EQE) as a function of host thickness shows a good fit with the long-range Förster interaction.*

Variation of the thickness of host layer reveals a new long range quenching mechanism involving a Förster-like dipole-dipole interaction. The quantitative analysis shows that the external quantum efficiency (EQE) as a function of host layer thickness follows the characteristic of the long range Förster process (Figure 2 b). To discuss the long-range quenching mechanism quantitatively, we plotted the EQE versus CBP thickness. It is known that the rate of the long range Förster process (K$_{Fnr}$) is proportional to R^{-6} for two-molecules interaction[4] and R^{-4} for molecule-planar layer interaction[5] where R is the distance between the donor and acceptor, i.e. the CBP thickness approximately. Hence, the EQE $\propto \left[1 + \left(R_{Fnr2D}/R\right)^4\right]^{-1}$, where R_{Fnr2D} is the modified 2D nonradiative Förster radius which is related to the nonradiative Förster radius $\left(R_{Fnr}\right)$ by $R_{Fnr2D} = \left(\sigma\pi R_{Fnr}^6\right)^{1/4}$,[6] where σ is the molecular surface density of the guest layer.

It can be seen from the inset of Figure 2b, the data obtained experimentally (square) show a sharp increase in EQE for CBP thickness larger than 3 nm, which agrees well to the fitting curve (solid line) with a 2D Förster-type decaying rate (R^{-4}). This further verifies that the excitonic quenching occurred for devices with thin layer of CBP are enabled by the long range dipole-dipole interaction. From the fitting, the modified 2D nonradiative Förster radius is found to be around 3.8 nm. Assuming that the molecular surface density of the 1 nm Ir(ppy)$_3$ guest layer is approximately $\sigma \approx 1 - 0.6^2$ nm^{-2}.[7] The nonradiative Förster radius $\left(R_{Fnr}\right)$ can be approximated to be 2.0-2.3 nm. This value is comparable to the calculated value of 1.8 nm for Ir(ppy)$_3$ based on spectrum overlap.[8] It is worth mentioning that device with bulk layer of Ir(ppy)$_3$, i.e. with R approaches the inter-molecular distance, EQE still show a respectable value of 0.6 % (shown in Figure 2b as $R = 0$).

4. Concentration-quenching in fluorescent host-guest system

To investigate the mechanisms responsible for concentration quenching in phosphorescent host-guest system devices were fabricated with a structure of NPB/ [DCM (0.1 nm)/ Alq$_3$ (y nm)] (6 cells)/ DCM (0.1 nm)/ BCP, where y was varied from 3, 6, 7, 8, 10, 15, to 20 nm.[9]

In Figure 3, we plotted the EQE versus the Alq$_3$ thickness. It can be seen that the data obtained experimentally (square) fits well with decaying rate R^{-4}, indicating that the excitonic quenching occurred for devices with thin layer of Alq$_3$ are enabled by the long range dipole-dipole interaction. From the fitting, the modified 2D radiationless Förster radius is around 6.5 nm.

$$\propto \frac{1}{1+\left(\dfrac{R_{Fnr2D}}{R}\right)^4}$$
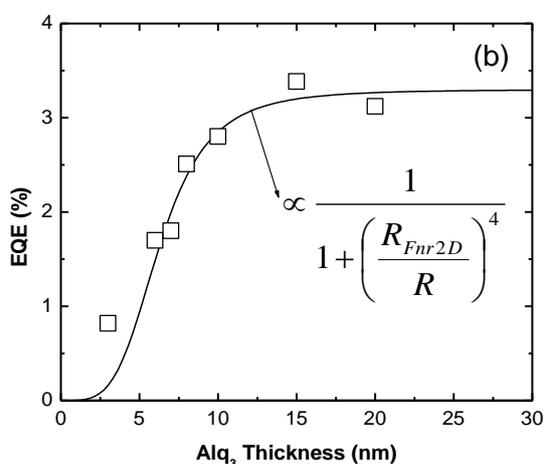
Figure 3 *EQE versus Alq$_3$ thickness (squares) and the fitting curve (solid line) utilizing the Förster-type quenching rate, with R_{Fnr2D} = 6.5 nm.*

5. Exciton Diffusion in Organic Semiconductor

Recently we studied the one-dimensional exciton diffusion in tris(2-phenylpyridine) iridium(III) molecules as a function of intermolecular spacing.[10] We showed for the first time the existence of an optimum intermolecular spacing that gives the longest diffusion length (L_D) in [Ir(ppy)$_3$] molecules. When the intermolecular spacing is too short, the long-range excitonic quenching becomes dominant; on the other hand, when it is too long, the exciton energy transfer is miniscule. A specially designed organic light-emitting diode with separate exciton formation and emission was constructed to measure the one-dimensional exciton diffusion length. The maximum one-dimensional exciton diffusion length for this material is around 8.5 nm for intermolecular separation of around 4.5 nm. Figure 4a shows the OLED structure used to investigate the exciton diffusion in Ir(ppy)$_3$, and Figure 4b shows the measured exciton diffusion length as a function of intermolecular spacing.
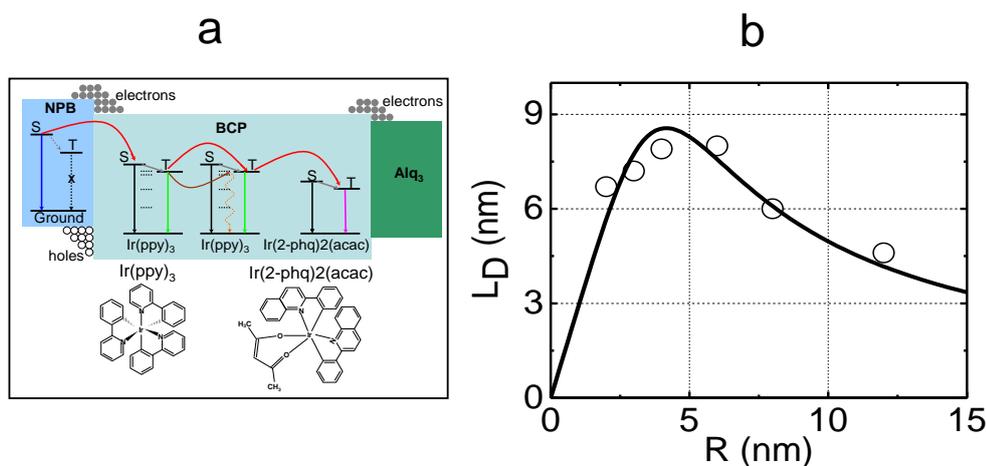
Figure 4. *a) Illustration of organic light-emitting diode (OLED) structure utilized to measure the exciton diffusion length (L_D) of Ir(ppy)$_3$ as a function of intermolecular-spacing. b) The measured L_D as a function of intermolecular-spacing.*

6. Conclusion

Organic semiconductor suffers from long-range Förster -like concentration quenching (QC). QC occurs in both phosphorescent and fluorescent molecus. The presence of QC produces a non-monotonous L_D profile as a function of intermolecular spacing. This result will have tremendous impact to the development of organic LED and photovoltaicdevices which rely heavily on exciton diffusion.

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