Exciton Dissociation in Organic Light Emitting Diodes at the Donor-Acceptor Interface

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Experimental *in situ* photoluminescence and transient photovoltage results show that the interface formed by N, N'-Bis(naphthalene-1-yl)-N, N'-bis(phenyl) benzidine (NPB) and tris(8-hydroxyquinoline) aluminum (Alq$_3$) acts as an exciton dissociation site. Because of this dissociation effect, excitons formed in NPB at or within a diffusion length of the interface tend to dissociate before they radiatively decay to generate blue light. This suggests that the action of the "hole-blocking layer" used in indium tin oxide\NPB\hole-blocking layer{Alq$_3${aluminium to promote blue light emission from the NPB is more "exciton dissociation inhibition" than "hole blocking."

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In the light-emission mechanism of indium tin oxide (ITO)\N, N'-Bis(naphthalene-1-yl)-N, N'-bis (phenyl) benzidine (NPB)\tris-8-hydroxyquinoline aluminum (Alq$_3$)\aluminum (Al), an organic light emitting diode (OLED), electrons and holes are injected from Al and ITO, respectively, and then excitons are formed in the Alq$_3$ which generate green light at their deexcitation [1]. An interesting phenomenon is that blue light is emitted from the NPB only when a thin layer such as bathocuproine (BCP) is interposed between the NPB and Alq$_3$ [2–4]. The role of this BCP layer is commonly interpreted to be hole blocking [2–4]. Under electroluminescence (EL) conditions and in the absence of this BCP layer, many holes should accumulate in the NPB at the interface with Alq$_3$ because of the barrier formed by the energy difference between the highest occupied molecule orbitals (HOMO) of NPB and Alq$_3$ [4,5]. There is thus already a barrier to hole propagation across the NPB/Alq$_3$ interface in the absence of a BCP layer. Thus it seems that the "hole-blocking layer" acts not solely (or even principally) as a hole blocker. Further explanation is needed for why no blue light from NPB is observed in the absence of such a hole-blocking layer.

When excitons reach or form at an interface between two different materials, their fate can be quite different from their fate in either of the bulk materials: radiative and nonradiative decays of the excitons are still possible, but they can also be transferred to the second material [6,7] or be dissociated by transfer of a charge quantum to the second material, leaving behind an opposite charge in the first material [8–12]. Interfaces in polymer solar cells [9,10] and those in small organic molecule solar cells [11,12] have proved to be very efficient exciton dissociation sites. A distinct feature of these interfaces is that the both HOMO and the lowest unoccupied molecule orbital (LUMO) are higher in one material than in the other, which is normally considered to be the necessary energy configuration for interfacial exciton dissociation [13,14]. Since the positions of HOMO and LUMO in NPB and Alq$_3$ have this configuration (Fig. 1, inset), it is a reasonable supposition that exciton dissociations can take place at the NPB-Alq$_3$ interface. If the exciton dissociation efficiency is high at the NPB-Alq$_3$ interface, the absence of blue light emission from the NPB can be explained as the result of this competitive nonradiative decay mode. The relative positions of HOMO and LUMO are regarded to be a necessary condition for exciton dissociation, but are not known to be a sufficient condition for dissociation efficiency high enough to suppress all radiative deexcitation [15,16]. The question of dissociation efficiency is a matter that calls for experimental investigation.

Through use of *in situ* photoluminescence (PL) and transient photovoltage (TPV) techniques, we prove in

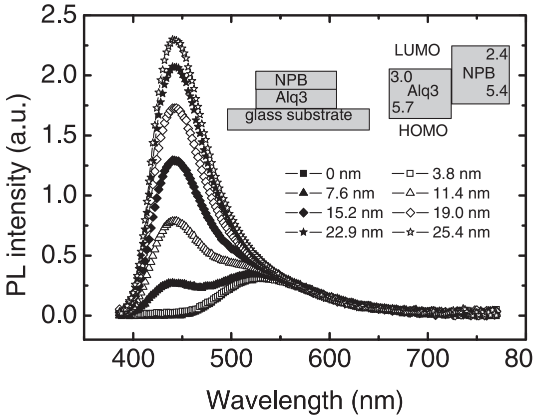

FIG. 1. PL spectra of sample A for several thicknesses of NPB under a cw laser illumination at a wavelength of 375 nm. The PL spectra were obtained at room temperature with a Photo Research PR705 spectroradiometer. The laser spot was elliptical (3.0 × 1.5 mm). For a description of the experimental procedure for *in situ* PL measurements, see Ref. [18].

this Letter that the excitons formed in NPB are efficiently dissociated at the NPB-Alq_3 interface. This explains the absence of EL from NPB in the absence of a thin BCP layer between the NPB and Alq_3; a BCP layer thicker than the exciton diffusion length (L_D) scale prevents the excitons from ''perceiving'' the NPB/Alq_3 interface and being deexcited at it. Our experiments also show that the interfacial exciton dissociation model is better than the band model.

The *in situ* PL of each sample was measured in a high vacuum ($\sim 3 \times 10^{-5}$ Pa) for 10 min while depositing organic materials. The PL intensity and the spectrum shape of 23.9 nm thick Alq_3 before and after 1.0 nm NPB deposition is identical (not shown here). This indicates that excitons in Alq_3 neither dissociate at nor propagate through the NPB-Alq_3 interface. We therefore confine our attention to excitons of NPB. PL for a number of thicknesses of NPB deposited on glass\Alq_3 (23.9 nm) are shown in Fig. 1 (sample A; the materials configuration is depicted in the inset). It is apparent in Fig. 1 that thin layers of NPB have unusually low PL compared with thicker layers. This is similar to the phenomenon observed for NPB on glass\gold (3.0 nm) substrate (sample B, not shown), in which the PL of the initial several nanometers thickness of NPB is quenched by the interface with the gold. The interference effect may modulate the incident light distribution in the NPB and the Alq_3 [17]. If interference is the only effect modulating the PL of NPB, then PL from the NPB should appear as soon as even the thinnest layer of NPB is deposited onto the Alq_3. This calculated result is shown in Fig. 2 along with the measured PLs of NPB and Alq_3. The PL intensity degradation of NPB and Alq_3 of sample A under laser irradiation is neglected in the calculation since degradation of only about 3% for NPB and less than 1% for Alq_3 in 10 min is observed (obtained by separately measuring the PL of 24.0 nm NPB and Alq_3 versus time). It is evident that there is negligible, and much less than predicted, PL from NPB films thinner than about 4.0 nm. This indicates quenching of NPB excitons by the NPB-Alq_3 interface. The missing NPB PL is plotted in Fig. 2, clearly demonstrating this quenching effect. A LD between 5.0 and 10.0 nm can be estimated by fitting PL versus NPB thickness T with formula (5) of the PL Ref. [18]. The fitted curve with $L_D = 4.9$ nm (using 4.9 ± 1 nm for NPB from Ref. [19]) is shown in Fig. 2. The fitting result is not very good, which may indicate that the boundary condition used (infinite quenching rate at the interface) is not valid for the NPB-Alq_3 interface. The measured PL versus T and the missing NPB PL may imply a complete deexcitation at the boundary, and thus a finite quenching rate at the NPB-Alq_3 interface means that some excitons of NPB at the interface are deexcited in other ways. For example, their energy can cause an excitation of the neighbor Alq_3 molecules, perhaps enhancing the Alq_3 light emission. They could also decay radiatively by recombination across the interface with an electron transfer from NPB to Alq_3 and a hole left on the NPB side (excimer deexcitation). The energy transfer to Alq_3 or excimer deexcitation would result in enhancement of the Alq_3 PL. Contrary to the predicted monotonic decrease of Alq_3 PL vs T, the observed PL of Alq_3 did increase slightly until the thickness of NPB reached about 9.0 nm, a scale similar to the estimated exciton L_D in NPB. This may indicate a small portion (less than 7%) of NPB excitons at the interface transfer their energy to the Alq_3, enhancing its light.

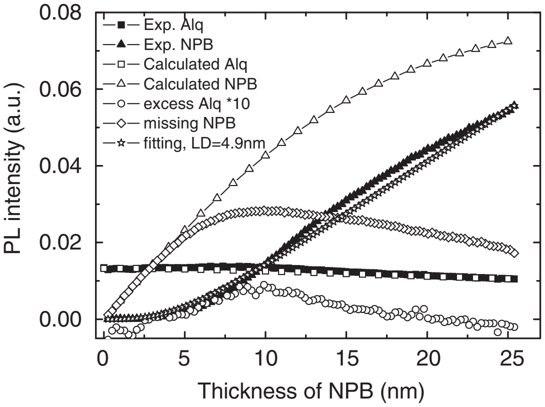

FIG. 2. PL intensity of NPB and Alq_3 of sample A versus NPB thickness. The fitting curve for PL of NPB is plotted with L_D of 4.9 nm. The calculated PLs of NPB and Alq_3 are based the transfer matrix method, and the PL intensity is considered proportional to the incident laser intensity absorbed by the organic layer. The calculated PLs are scaled to the measured PL of the same thickness of pure NPB or Alq_3 on glass. The excess PL of Alq_3 is obtained by subtracting measured PL from calculated PL; the displayed result has been multiplied by 10. The missing PL of NPB is obtained by subtracting calculated PL from measured PL.

As we expected, the *in situ* PL of Alq_3 deposited on glass\NPB (23.5 nm) substrate (sample C) shows that the PL of NPB decreases when Alq_3 is introduced due to exciton dissociation at the interface. A more interesting phenomenon is that the PL of Alq_3 does not increase monotonically with its thickness. In our experiments, the PL of Alq_3 increased rapidly in the first 1.3 nm, then decreased until ~6.0 nm, and thereafter increased almost linearly with increasing Alq_3 thickness. The normalized variation of PLs for Alq_3 and NPB of sample C versus the thickness of Alq_3 is shown in Fig. 3. The results for Alq_3 interaction with the NPB-Alq_3 show that this is not a sink of Alq_3 excitons. The predicted Alq_3 PL versus T under the assumption that there is no energy source other than the incident laser light modulated by interference is shown in Fig. 3 (filled triangles). The large discrepancy between this prediction and the measured curve indicates that additional Alq_3 excitons are being generated somehow, and the only available source is the NPB substrate. The dissociation of excitons into free carriers at an organic-organic interface takes place in two steps [15,20–22]: a short geminate pair of carriers (SGP) is formed with the electron localized in an acceptor molecule and the hole occupying a donor molecule. Thereafter the SGP is further separated

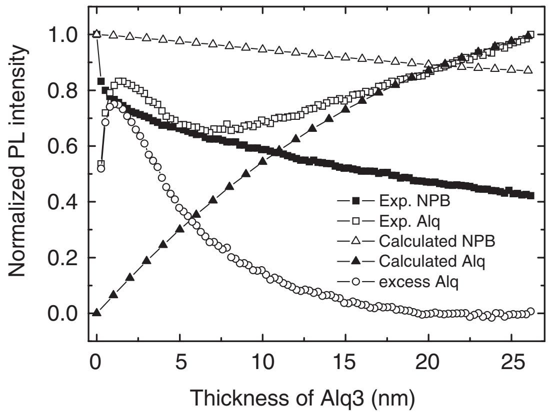

FIG. 3. Normalized PL intensity of $\mathrm{Alq_3}$ and NPB of sample C versus the thickness of $\mathrm{Alq_3}$. The excess PL of $\mathrm{Alq_3}$ is obtained by subtracting measured PL from calculated PL of $\mathrm{Alq_3}$. The calculation is based on the same method used in Fig. 2.

to a free electron and a free hole. The SGP separation can be as large as 3.1 nm for poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT) and poly(9,9-dioctylfluorene-co-bis-*N*, *N*′-(4-butylphenyl)-bis-*N*, *N*-phenyl-1, 4-phenylenediamine) (PFB) blend polymer [15].

SGPs are also produced at the NPB-$\mathrm{Alq_3}$ interface, and this can explain the observed $\mathrm{Alq_3}$ PL "bump" (Fig. 3). Before the monolayer (about 0.8 nm [6]) is formed during the deposition, every new $\mathrm{Alq_3}$ molecule deposited on NPB is a potential site for SGP formation. Thus, the SGP should be proportional to the fractional $\mathrm{Alq_3}$ coverage on the NPB when the thickness of $\mathrm{Alq_3} \ll 1.0$ nm. SGPs formed during this stage of $\mathrm{Alq_3}$ deposition have a long lifetime due to the insignificant charge mobility on the $\mathrm{Alq_3}$ side, resulting in an excimer deexcitation contribution to PL of $\mathrm{Alq_3}$ that is proportional to the amount of $\mathrm{Alq_3}$ in contact with NPB; this is the rapid linear increase seen in the lowest T data points. As notional full coverage is approached, the newly deposited $\mathrm{Alq_3}$ molecules tend to land preferentially on the first layer of $\mathrm{Alq_3}$ molecules rather than on the remaining patches of exposed NPB. Therefore, the number of available sites and the rate of creation of new SGPs increase less rapidly with $\mathrm{Alq_3}$ thickness. At this stage, prior to but approaching the full monolayer of $\mathrm{Alq_3}$, the charge mobility on the $\mathrm{Alq_3}$ side is still poor and the SGP lifetime is long; the $\mathrm{Alq_3}$ PL continues to increase, but less rapidly than before. The growing light contribution from excimer deexcitation to produce a blueshift effect is expected when the spectrum of $\mathrm{Alq_3}$ is obtained by subtracting the light from NPB. Such a blueshift (about 10.0 nm) is observed for 1.0 nm $\mathrm{Alq_3}$ on 23.5 nm NPB in comparison to the spectrum of pure $\mathrm{Alq_3}$ (not shown here). After a monolayer is formed, there is no further increase in the number of SGP formation sites and the charge mobility on the $\mathrm{Alq_3}$ side increases with the deposited $\mathrm{Alq_3}$ thickness, resulting in a decrease in the rate of excimer deexciation due to an increasing rate of destruction of SGPs by charge migration. Once the $\mathrm{Alq_3}$ layer is thicker than the characteristic size of the SGPs, which is estimated to be 4.9 nm from the half decrease of the excess PL of $\mathrm{Alq_3}$, the charges on the $\mathrm{Alq_3}$ side can simply wander freely into the bulk material and the SGPs are rapidly separated into free charges in the bulk NPB and $\mathrm{Alq_3}$. Therefore, very little of the energy in these pairs is available for excimer deexcitation at the interface. After 4.9 nm, the PL variation of $\mathrm{Alq_3}$ mainly comes from bulk material PL in the increasing thickness of $\mathrm{Alq_3}$, and it finally approaches to the calculated trend as shown in Fig. 3.

It is worthy of note that the excitation wavelength of the laser used in these PL experiments was 375 ± 5 nm, at which the extinction coefficients for NPB and $\mathrm{Alq_3}$ (0.125 and 0.109, respectively) are almost the same and thus both NPB and $\mathrm{Alq_3}$ are excited. More information, such as the distribution of separation distances of short geminate pair of carriers could be obtained by investigation of PL under different excitation wavelengths.

Both the PL decrease of NPB for $\mathrm{Alq_3}$ on NPB and the absence of NPB PL from thin NPB layers on $\mathrm{Alq_3}$ could alternatively be explained as PL quenching by interface states introduced by the second material deposited on the first one. This type of quenching can only produce heat, while interface exciton dissociation can produce measurable TPV [23,24]. Accordingly, we used TPV to distinguish the quenching between interface states from that caused by exciton dissociation at the NPB-$\mathrm{Alq_3}$ interface. Figure 4(a) shows measurements of TPVs in sample D and sample E (the materials configurations are depicted in the insets). It is clear that the polarity of the transient voltage is not changed by the inhibition of exciton dissociation at the ITO-organic interface that is produced by the insulator layer of LiF [23]. The observed TPV in Fig. 4(a) has two sources. One source is the motion of a free hole (electron) and free electron (hole) to the ITO (Al) side in sample D and to the Au (ITO) side in sample E driven by the electric field ($\mathrm{E_{bi}}$) between the two electrodes. Another source is the exciton dissociation at the NPB-$\mathrm{Alq_3}$ interface, which transfers an electron to the $\mathrm{Alq_3}$ and leaves a hole in the NPB. This would impose a TPV with the same polarity at that produced by $\mathrm{E_{bi}}$, resulting in an overshoot in the final observed TPV [Fig. 4(a)]. Since the interface dissociation is independent of $\mathrm{E_{bi}}$, change of the deposition sequence in sample D and sample E would change the polarity of TPV produced in NPB-$\mathrm{Alq_3}$ interface dissociation. TPV controlled by the interfacial dissociation and then by $\mathrm{E_{bi}}$ would result in a polarity change in the final observed transient photovoltage [Fig. 4(b)]. These TPV measurements decisively confirm that the PL quenching is due to exciton dissociation at the NPB-$\mathrm{Alq_3}$ interface.

Our experimental findings that excitons in NPB dissociate at NPB-$\mathrm{Alq_3}$ interfaces provide a clear explanation of why there is no blue light generated from bilayer OLEDs of ITO\NPB\$\mathrm{Alq_3}$\Al. Under EL conditions, electrons and holes are injected from Al and ITO, respectively. Because of the energy barriers at the NPB-$\mathrm{Alq_3}$ interface,

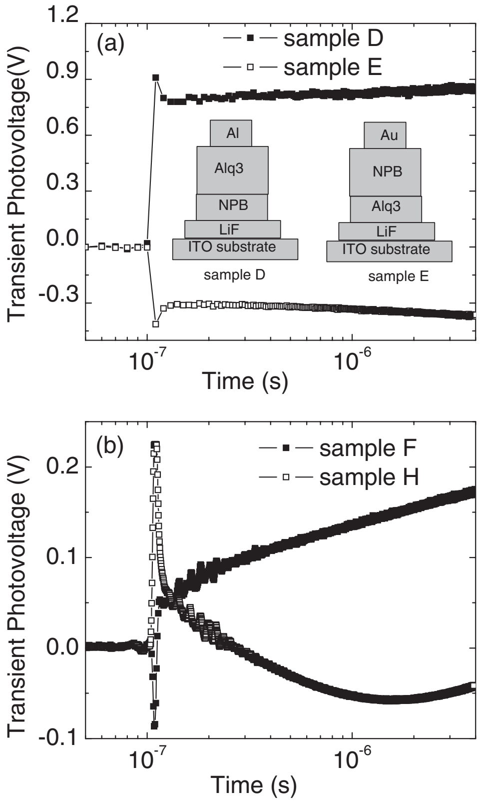

FIG. 4. TPVs of (a) ITO\LiF(10 nm)\NPB(10 nm)\$Alq_3$(600 nm)\Al (sample D) and ITO\LiF(10 nm)\$Alq_3$(10 nm)\NPB(700 nm)\Au (sample E), (b) ITO\LiF(10 nm)\$Alq_3$(10 nm)\NPB(700 nm)\Al (sample F) and ITO\LiF(8 nm)\NPB(10 nm)\$Alq_3$(1000 nm)\Au (sample H). TPV was measured by illuminating the device from the ITO side, with the metal electrode grounded (see Ref. [23]). The wavelength of the pulse laser (duration of 3–7 ns) was 355 nm, triple harmonic from Nd:YAG laser. 3.33 Hz repetition rate was used. The photo voltage signals were collected with a Tektronix TDS3012B oscilloscope with 100 MHz band width. All measurements were made in air at room temperature.

excitons for Alq_3 and NPB are mainly formed near this interface. Green light from Alq_3 is emitted because the excitons of Alq_3 do not dissociate at the interface, while blue light from NPB is not emitted because of the interface dissociation of the NPB excitons. Due to the quite large (about 4.9 nm) separation of short geminate carriers, the layer between the NPB and Alq_3 should be much larger (above 10 nm [2,4]) to efficiently inhibit the exciton dissociation; this will result in bright blue light emission from the NPB.

Our work shows that PL quenching occurs prior to the formation of an Alq_3 monolayer, a physical situation in which band bending is impossible. PL quenching is generally attributed to exciton dissociation. Therefore, our results favor the interfacial model of exciton dissociation [8,25] over the band model [21,26]. Since the free carriers are controlled by interfacial dissociation, control of the interface is very important for organic solar cells [27].

In summary, *in situ* PL and TPV studies show that NPB-Alq_3 interface is an efficient dissociation site for NPB excitons. Due to the exciton dissociation effect, excitons formed in NPB at the interface and those near the interface within the L_D are preferentially dissociated, resulting in suppression of blue light emission (radiative decays). Under EL conditions, excitons of NPB are mostly formed near the NPB-Alq_3 interface, within the diffusion length for excitons in NPB (under PL conditions). Thus, without the so-called hole-blocking layer in diodes of ITO\NPB\hole blocking layer\Alq_3\aluminum to prevent interface exciton dissociation, no blue light is emitted from the NPB as the great majority of the excitons are dissociated at the interface before they can radiatively deexcite. Our experiments strongly support the interface exciton dissociation model.

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