Electron blocking and hole injection: The role of N,N'-Bis(naphthalen-1-y)-N,N'-bis(phenyl)benzidine in organic light-emitting devices

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The current density-luminance-voltage characteristics of organic light-emitting devices (OLEDs) with N,N'-Bis(naphthalen-1-yl)-N,N'-bis(phenyl) benzidine (NPB) of various thicknesses as the hole transport layer have been investigated. It is found that for conventional structures of indium–tin–oxide/NPB/tris(8-hydroxyquinoline) aluminum (Alq_3) (60 nm)/LiF (0.5 nm)/Al the optimal hole injection and luminescence efficiencies appear at NPB thicknesses of 5 and 20 nm, respectively. The large difference between the two optimal thicknesses suggests that the effective block of the NPB layer against electrons from across the Alq_3/NPB interface is essential for high-efficiency operation of the OLEDs. The electron blocking effect of NPB is further confirmed by the electroluminescence (EL) behavior of devices with the structure of ITO/NPB(5 nm)/Alq_3:4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM) (30 nm)/NPB/Alq_3(60 nm)/LiF(0.5 nm)/Al. The proportion of DCM EL to the whole EL decreases with increasing NPB thickness. This suggests that the NPB layer blocks electron transport to the Alq_3:DCM layer. The Förster energy transfer from the 60 nm Alq_3 layer to the DCM molecules is ruled out by the EL behavior observed after quenching excitons in the Alq_3 layer. The origin of the difference in the optimal N,N'-Bis(3-methylphenyl)-N,N'-bis(phenyl)benzidine (TPD) thicknesses reported by other two different groups is also discussed. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1699472]

Since Tang *et al.* reported highly efficient organic light-emitting devices (OLEDs) with novel multilayer structure,[1] much attention has been devoted to the research of the physical and chemical properties of OLEDs.[2–4] In Tang's work, a N,N'-Bis(3-methylphenyl)-N,N'-bis(phenyl)benzidine (TPD)-like diamine serves as a hole transporting layer which enhances the hole injection and increases the quantum efficiency dramatically. Qiu *et al.*[5] studied the dependence of the turn-on voltage and luminescence efficiency on the TPD thickness. According to their results, thickness of 40 nm or larger is usually adopted for the TPD layer. However, because of its low glass transition temperature (T_g), TPD has now been replaced by N,N'-Bis(naphthalen-1-yl)-N,N'-bis(phenyl)benzidine (NPB), whose T_g is about 20° higher.[6] The optimal thickness of TPD, 40 nm or larger, is usually considered adoptable for NPB,[6–8] but the validity of the idea has not been proved experimentally. Furthermore, despite of the wide usage, the effect of NPB insertion on electron process has not been fully understood so far.

In this work, by comparing the device performances with NPB of different thicknesses, it is found that the optimal thickness is much smaller than that usually used. The electron blocking effect of NPB is directly observed in our electroluminescence (EL) measurements and the validity of the NPB's optimal thickness is confirmed. The EL measurement of devices with metal-doped tris(8-hydroxyquinoline)

aluminum (Alq_3) excludes the possibility of Förster energy transfer.

All the devices were fabricated and measured in the way described in Ref. 8. The first device structure was ITO/NPB/Alq_3(60 nm)/Al, with the NPB thickness varying from 0 to 60 nm. The measured V–J and L–J characteristics of the devices are shown in Fig. 1. It is seen that, because of the great enhancement of hole injection, the insertion of NPB initially shifts the V–J curves toward lower turn-on voltage. But for NPB thickness greater than 5 nm, due to the lowering of the electric field strength, this trend reverses. Because of the poor electron injection ability of the Al cathode and the small thickness of Alq_3, the electron current here is expected to be injection limited[3] and the hole injection will have no great impact on electron injection except that the insertion of NPB will decrease the electric field strength in the Alq_3 layer under a certain voltage. But due to the relatively high carrier mobility in NPB,[9] little voltage will be expected to drop across the NPB layer[10] and the change in electric field in Alq_3, and thus the change in electron current, are negligible. This means that a 5-nm-thick NPB layer is sufficient to achieve the maximum hole injection and thicker NPB will only decrease the internal electric field and hence the overall current. Devices with the structure of ITO/NPB/Alq_3(60 nm)/LiF(0.5 nm)/Al present a little different V–J characteristics from devices without LiF [see Fig. 2(a)]. The optimal thickness is 3 nm and the magnitude of current density increasing at the same voltage is much larger. This is because the Al/LiF cathode has much better electron injection ability[3] and the current is space charge limited rather than injection

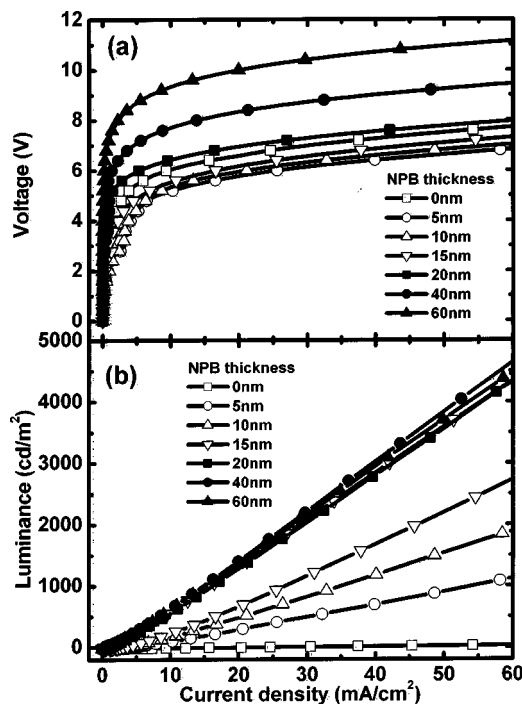[a]Author to whom correspondence should be addressed; electronic mail: xyhou@fudan.edu.cn

FIG. 1. (a) $V-J$ and (b) $L-J$ characteristics of devices with the structure of ITO/NPB/Alq(60 nm)/Al. The symbols are as follows: open square, open circle, open triangle, open inverted triangle, closed square, closed circle, and closed triangle represent the NPB layer thicknesses of 0, 5, 10, 15, 20, 40, and 60 nm, respectively.
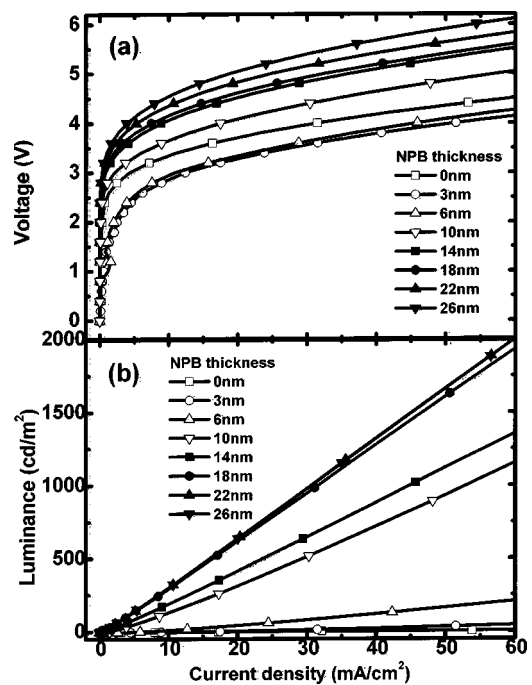

FIG. 2. (a) $V-J$ and (b) $L-J$ characteristics of devices with the structure of ITO/NPB/Alq(60 nm)/LiF(0.5 nm)/Al. The symbols are as follows: open square, open circle, open triangle, open inverted triangle, closed square, closed circle, closed triangle, and closed inverted triangle represent the NPB layer thicknesses of 0, 3, 6, 10, 14, 18, 22, and 26 nm, respectively.

limited.[11,12] The hole injection will facilitate the electron transport and the overall increase of current includes both the hole injection and the resulting increase of electron current. The change in the overall current is much more complicated than that without LiF. So the change in the current of the first device reveals the true effect of the NPB insertion on the hole injection. The optimal NPB thickness for hole injection is preferably 5 nm, which is much smaller than that usually expected, though the exact value may be a little different because the step of the NPB thickness increasing is several nanometers.

The $L-J$ curves exhibit quite different characteristics. The values of luminance of both devices increase with the NPB thickness monotonously until it approaches 20 nm [see Figs. 1(b) and 2(b)]. However, according to the above analysis, the hole injection becomes saturated once the NPB thickness reaches 5 nm. We attribute this further increase in efficiency with the NPB thickness beyond 5 nm to the electron blocking effect of NPB. Similar effect of TPD has been reported by Yang *et al.*[13] They fabricated devices having a structure of ITO/PPV/TPD/Alq$_3$:4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM)/Al and found that a 10 nm TPD layer could completely block electron transport from Alq$_3$:DCM to PPV.

To test whether the electrons are blocked by NPB, we fabricated devices having the structure of ITO/NPB(5 nm)/Alq$_3$:DCM(30 nm)/NPB/Alq$_3$(60 nm)/LiF(0.5 nm)/Al, with the thickness of NPB between the Alq$_3$ and Alq$_3$:DCM layers varying from 0 to 50 nm. The doping ratio of DCM is 1.7% by weight. In the measurement of the EL spectra of the devices, both green light from Alq$_3$ and red light from DCM were detected. The inset of Fig. 3 shows the spectrum of a

device with 10-nm-thick inserted NPB at a current density of 10 mA/cm^2. We fit this spectrum by the EL spectra of DCM and Alq$_3$ with their peak ratio (σ) of 1.27, and define the proportion of DCM EL to the whole EL, η, as $\sigma/(\sigma+1)$, labeled as $I_{DCM}/(I_{DCM}+I_{Alq})$ in Fig. 3. Because the Alq$_3$:DCM layer is adjacent to the anode-connected NPB layer and is then hole-rich, the DCM EL should be proportional to the amount of electrons that traverse the other NPB layer. It should be pointed out here that, because of differences in the spectrum line shape and quantum efficiency between Alq$_3$ and DCM, η does not equal the proportion of electrons traversing the NPB layer to the whole electrons
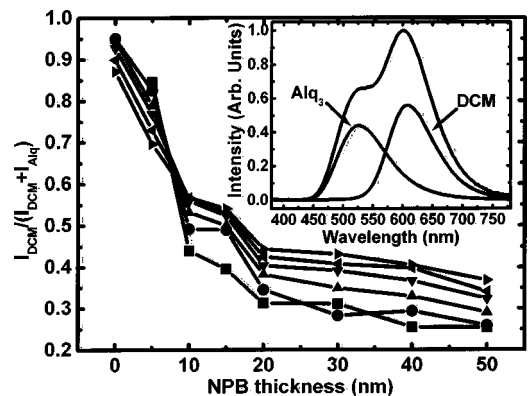

FIG. 3. The proportion of DCM EL to the whole EL vs the NPB thickness of devices having a structure of ITO/NPB(5 nm)/Alq$_3$:DCM(30 nm)/NPB/Alq$_3$(60 nm)/LiF(0.5 nm)/Al. The symbols represent different current densities: 0.15 mA/cm^2 (square), 0.6 mA/cm^2 (circle), 2.4 mA/cm^2 (triangle), 10 mA/cm^2 (inverted triangle), 40 mA/cm^2 (left triangle), 160 mA/cm^2 (right triangle). The inset shows a measured EL spectrum with the NPB thickness of 10 nm at the current density of 10 mA/cm^2 and its component spectra of DCM and Alq$_3$.
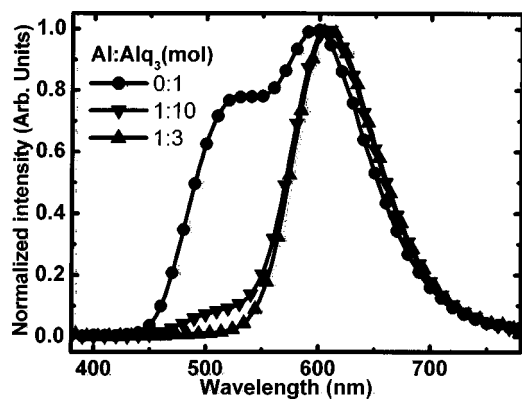
FIG. 4. EL spectra of devices with the structure of ITO/NPB(5 nm)/ Alq_3:DCM (30 nm)/NPB(15 nm)/Alq_3:Al(60 nm)/LiF(0.5 nm)/Al with different molar doping ratios of Al to Alq_3: 0:1 (circle), 1:10 (inverted triangle) and 1:3 (triangle).

injected into the device, though they are positively correlated. Figure 3 shows the variation in η with the thickness of NPB inserted. It could be seen that the proportion decreases sharply with NPB thickness at the beginning, and then changes little for thickness beyond 20 nm. This means that NPB thicker than 20 nm could have no obvious further blocking effect for electrons. This result gives a good explanation of the optimal thickness at 20 nm for luminescence efficiency.

Another possible explanation of DCM EL is the Förster energy transfer from the 60 nm Alq_3 layer to the doped DCM molecules. Inserting NPB between Alq_3 and Alq_3:DCM layers will decrease the energy transfer rate,[14] leading to the similar variation of EL feature. To test this possibility, we doped the 60 nm Alq_3 layer with Al atoms, which could greatly quench the excitons in Alq_3. Devices with Alq_3 doped with Al atoms of 0%, 10%, and 33% molar ratios were fabricated and their EL spectra were measured. If the DCM EL results from the energy transfer from excitons in the Alq_3 layer, which is also the source of Alq_3 EL, the DCM EL intensity should be proportional to the EL intensity of Alq_3. So the quench of excitons will depress the EL intensities of DCM and Alq_3 proportionally, i.e., the spectrum line shape of the devices should keep unchanged. Figure 4 shows that this is obviously not the case. The doping of Al atoms has a much stronger effect on the EL of Alq_3 than that of DCM, although both the intensities are reduced greatly. The doping of Al atoms will affect the carrier injection, transporting, and recombination of excitons. All these effects might cause the reduction in the EL intensity, but will not change the intensity ratio of DCM to Alq_3 if DCM EL is caused by the Förster energy transfer.

It is noteworthy that the minimum η, with the NPB layer as thick as 50 nm, is not zero but near 30% (see Fig. 3). This indicates that there are still many electrons escaping from the organic layers without recombination with holes in the conventional structure and that by optimizing the structure properly the efficiency can be improved further. It can also be seen from Fig. 3 that η at different current densities exhibit different variation features. The mechanism needs to be further explored.

Here the optimal thickness for luminescence efficiency

and the largest effective thickness for electron blocking are identical. But the optimal thickness, 40 nm, of TPD in Ref. 5, differs from the effective thickness, 10 nm, for blocking electrons reported in Ref. 13. We ascribe the inconsistency to the structural difference between the devices in their experiments. In the case of Ref. 13, the electron injection by an Al cathode is poor, and Alq_3:DCM layer has a high exciton recombination efficiency. As a result, almost all electrons are exhausted by recombination with holes and very few electrons can reach the PPV layer and a very thin TPD layer will make the PPV EL undetectable. This special structure in Ref. 13 makes the optimal thickness smaller than that in conventional experiments.

In summary, by studying current and luminance characteristics of OLEDs with NPB of different thicknesses, we have found that a 5-nm-thick NPB layer could effectively enhance the hole injection and that the optimal thickness for luminescence efficiency is about 20 nm. The efficiency increasing with NPB thickness beyond 5 nm is attributed to the electron blocking effect of NPB, which is directly observed by EL measurement of devices with DCM whose EL intensity is representative of the amount of the electrons traversing the NPB layer. The optimal efficiency thickness, 20 nm, fits well with the results in the EL measurement. Possible Förster energy transfer is ruled out by analyzing the EL spectra of the devices doped with Al atoms. The disagreement between the two optimal thicknesses reported by two different groups is also explained.

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