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Exciton Migration and Cathode Quenching in Organic Light Emitting Diodes[†]

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The quantum efficiency of organic light emitting devices depends on the exciton emission efficiency. Exciton quenching at the metal cathode can be responsible for lowering the device performance. We consider exciton quenching by the metal cathode, taking into account both exciton diffusion and radiationless energy transfer to the metal. The quenching effect in tris(8-hydroxyquinoline)aluminum is analyzed, and ways to improve the device efficiency by suppressing the interaction with the electrode are discussed.

I. Introduction

Organic light emitting diodes (OLEDs) are low cost electronic devices using organic molecules (for review see ref 1−5 and references cited therein). They produce light of well-defined color upon application of voltage across electrodes having an organic emissive layer between them. This happens because electrons and holes, injected into an emissive layer, form molecular excitons that can decay with the emission of light. The energy of emitted photons corresponds to the first excited singlet state energy of organic molecules forming the emissive layer.

Complete theoretical understanding of the whole set of relevant processes in OLEDs is challenging because of their complexity. Actually, the performance of OLEDs depends on many factors. Most important are the efficiency of electron−hole recombination with respect to the lossy leakage channel, and the emission efficiency in comparison with radiationless decay for the excitons. There are many experimental and theoretical studies devoted to the analysis of the recombination efficiency (see, e.g., refs 6−8). They generally lead to the conclusion that it can be as high as unity if the electron injection is sufficient. Control of the injection efficiency by changing the metal electrode's work function yields stable and highly efficient devices with nearly perfect recombination efficiency.[9] The emission efficiency of excitons has also attracted much attention. The most significant channels of radiationless exciton decay competing with the light emission include intersystem crossing to the triplet states which decay usually without light emission (see refs 10 and 11 and references cited therein), exciton dissociation caused by the applied electric field,[12,13] and exciton quenching at external or impurity quenching centers. The latter process is particularly important when the emissive layer has a common boundary with the metal, where exciton energy can be transferred to excite electron−hole pairs. The analysis of photoluminescence quenching for the widely used light emitting materials such as tris(8-hydroxyquinoline)aluminum (Alq_3)[14] and 1,4-bis[4-(3,5-di-*tert*-butylstyryl)styryl]benzene (4PV)[15] shows remarkable quenching by various metals for organic layer thickness of about 30 nm, which is close to the practically used thickness, 50 nm (see, e.g., ref 8). The strong dependence of the emission efficiency on the thickness of the emissive layer for one of the most successful and stable configurations of the Alq_3 emissive layer with an Al cathode[16] also argues for the significance of quenching.

To the best of our knowledge a complete theoretical analysis of the quenching of excitons due to the interaction with the metal, taking into account the specific light emitting materials used in OLEDs, has not yet been performed. We outline such an analysis and apply the results to quenching in devices based on an Alq_3 emissive layer. Some suggestions for improving device performance by suppression of quenching are made.

Two issues are important to describe the exciton quenching by the metal interface. The first is the process of the irreversible energy transfer from the excited molecule to the metal; this is governed by the long-range dipole−dipole interaction. It has been described within the classical energy transfer theory developed by Chance, Prock, and Silbey more than 20 years ago.[17] This theory gives perfect qualitative and reasonable quantitative agreement with the experimental data and agrees[16] qualitatively with the thickness dependence of the emission efficiency in Alq_3.

The second issue is exciton diffusion. The exciton can diffuse closer to the metal interface, which makes the radiationless energy transfer efficiency higher than for localized excitons. The singlet exciton diffusion length in Alq_3 has been estimated as about 20 nm according to the experimental data of refs 14 and 18.

In this paper we develop a theory considering both exciton diffusion and quenching due to interaction with the metal. The model is formulated in section II. In section III the experimental data for exciton quenching are analyzed for an Alq_3 emitter. We consider the dependence of the emission efficiency on the various device parameters to formulate suggestions to enhance emission efficiency. Conclusions appear in section IV.

II. Model for Exciton Migration and Quenching

We consider singlet excitons formed on organic molecules of the emissive layer, occupying a slab of thickness t_s (usually between 10 and 100 nm) in contact with the metal boundary on the left side (see Figure 1). This contact might be direct (Figure 1a) or through some intermediate dielectric material of thickness t_{int} inserted between the metal and the emissive layer (Figure 1b). The distance between the reference emissive molecule and the metal is described by transverse coordinate

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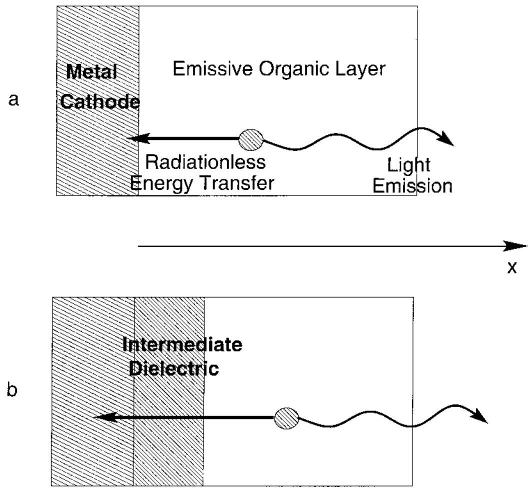

Figure 1. An emissive layer of OLED, contacting with a metal (a) directly or (b) through an intermediate layer. The arrows illustrates decay channels for a singlet excited molecule (exciton).

x. We assume that the density of excitons and carriers in the emissive layer is low enough that interexcitonic interaction can be neglected. The current in the most efficient devices (see, e.g., refs 19−21) is about several hundreds milliamperes per square centimeter, which corresponds to the creation of about one exciton in 10^{-21} m^3 during the exciton lifetime (about 10^{-8}−10^{-9} s for radiative decay). Accordingly the average distance between excitons is about 100 nm, which is larger than their diffusion length of 20 nm. The characteristic dipole−dipole interaction of excitons at that distance can be estimated as 10^{-6} eV, so it also can be neglected. This estimate proves the validity of the independent exciton picture.

The evolution of a singlet exciton located on molecule i can be described by the rate equation for the survival probability P_i

$$\frac{dP_i}{dt} = -rP_i - r_{me}P_i + s \tag{1}$$

where the rate constants for radiative decay and quenching due to the metal are denoted r and r_{me} respectively and s represents the external source, creating excitons by external photoexcitation or by electron−hole pair collisions for electroluminescence. Both r_{me} and s can depend on the distance x to the electrode. For instance, for photoexcitation the source term is independent of x, while for electroexcitation it depends on the location where the recombination of electrons and holes mostly occurs. Some theoretical models (see, e.g., ref 6) suggest that it predominantly occurs near the emissive layer boundaries.

The x dependence of the nonradiative decay rate constant r_{me} has been studied in ref 17, where a general expression has been derived within classical light reflection theory. For the case of interest corresponding to distance between emissive molecule and metal small in comparison with the resonant wavelength, it shows x^{-3} dependence[22]

$$r_{me} = r\frac{3}{32}\frac{\lambda^3\Theta}{\pi^3 n_1}\frac{n_2K_2}{(n_1^2 + n_2^2 - K_2^2)^2 + 4n_2^2K_2^2}\frac{1}{x^3} \tag{2}$$

Here r is the radiative decay rate constant for dipole transition, λ is the resonant wavelength, and Θ is a geometric factor for the different orentations of molecule with respect to the metal. We replace it with its mean value $^4/_3$ [17] in future calculations. n_1 is the refractive index of the media, while $n_2 + iK_2$ represents the complex reflective index of the metal with the imaginary part K_2 responsible for energy absorption. All refractive indexes are taken at the resonant frequency $\omega_0 = 2\pi c/\lambda$. At such a high frequency the dielectric constant of organic material is close to 2 and the refractive index is taken as $n_1 \approx \sqrt{2}$. For the characteristic parameters of the metal given in ref 17 and exciton wavelength $\lambda \sim 500$ nm, one can approximate expression eq 2 as

$$r_{me} = r\frac{x_0^3}{x^3} \tag{3}$$

with $x_0 \sim 10$−20 nm (see below). Accordingly molecules separated from the metal by a distance longer than x_0 decay mostly radiatively, while molecules located closer transfer their energy to the metal. While eq 2 cannot be used for very short distances $x \sim 0.1$ nm, most material effect is defined by the longer lengths close to x_0, where eq 3 is definitely applicable.

This model for quenching assumes that the bulk properties of the metal are responsible for the quenching effect. An alternative model considers the formation of special surface compound states composed from the metal ions and emissive layer molecules at the boundary with the metal; these can contribute to quenching as well.[23] However, these states produce a transfer rate decreasing with the distance as x^{-4} (cf. ref 17). At sufficiently long distance energy transfer to the bulk of the metal, scaling as x^{-3} should dominate. In particular x^{-3} distance dependence of the emission efficiency has been found in Alq$_3$[16] for $x > 10$ nm. Moreover, this dependence is confirmed in many other materials (see, e.g., ref 17 and references cited therein) for a similar distance range. Therefore we assume that the quenching mechanism eq 2 dominates for the relevant length scales for 50 nm emissive layers.

When the emissive layer is separated from the metal by a dielectric layer (Figure 1b), the expressions for the transfer rate eqs 2 and 3 have to be modified due to the difference in dielectric constants. If the intermediate dielectric layer is organic, then it has dielectric properties similar to those of the emissive layer. The only significant modification here is the constraint of the lowest possible distance between excited molecule and the metal by the thickness of that layer t_{int}. If the intermediate layer is inorganic, it might have a meaningfully different dielectric constant. If that dielectric constant is much greater than the dielectric constant of the emissive layer $\epsilon_\infty \approx 2$, one would expect that the energy transfer rate to the metal becomes smaller because of the suppression of the electrostatic interaction of exciton with the metal.

As we earlier mentioned, exciton motion can reduce the emission efficiency since the exciton can move closer to the metal. Consider the migration of excitons. We analyze this process within the classical diffusion formalism

$$\frac{\partial P}{\partial t} = D\frac{\partial^2 P}{\partial \mathbf{r}^2} \tag{4}$$

where $P(\mathbf{r},t)$ expresses the average exciton density at the position $\mathbf{r}$ and time t. Several comments concerning the nature of the approach eq 4 have to be made before applying it.

If we have two molecules i and j and molecule i is excited while molecule j is in the ground state, the exciton may jump to molecule j. This process can be described by the rate equations

$$\frac{dP_i}{dt} = -w_{ji}P_i + w_{ij}P_j$$
$$\frac{dP_j}{dt} = -w_{ij}P_j + w_{ji}P_i \tag{5}$$

where w_{ij} and w_{ji} express the hopping rates from molecule j to molecule i and backward, respectively. These transfer rates vary with the distance between molecules R_{ij} as

$$w_{ij} \propto \frac{1}{{R_{ij}}^6} \tag{6}$$

which expresses the Forster law[13,24] of exciton hopping due to the dipole−dipole interaction.

For the molecules within the organic emitting layer, one can then describe exciton migration as

$$\frac{dP_i}{dt} = \sum_j (w_{ij}P_j - w_{ji}P_i) \tag{7}$$

which is the traditional approximation to the problem (see, e.g., ref 13). One remark should be made here. The approximation leading to the rate equations (7) is derived from the application of the Fermi Golden rule to molecular pairs coupled by the dipole−dipole interaction. Processes involving more than two molecules were neglected. This means that the resonant coupling of molecules is weak in comparison with their energy dispersion, and collective excitations[25,26] can be neglected. It is not clear whether these assumptions are correct. The diffusion approximation eq 4 suggests that the length scales of the problem are greater than the size of collective excitations. While analysis in detail is hampered by insufficient knowledge of exciton parameters, the analysis of interference effects might be interesting for future study.

It is not straightforward to proceed from the master equation eq 7 to the diffusion equation eq 4. The reason is energy disordering (inhomogeneous broadening) of molecular levels. The exciton transition rates should satisfy detailed balance

$$w_{ij} = w_{ji} \exp\left(-\frac{E_i - E_j}{k_B T}\right) \tag{8}$$

Here E_i and E_j are the energies of exciton states at molecules i and j. Usually the emissive layer is disordered, and therefore the energies of the states must be distributed. Let w be the width of the energy distribution. If it is greater than the thermal energy k_BT, then the exciton is usually captured at the molecules with low energy (traps). The system can be described in terms of an effective diffusion coefficient resulting from averaging of rate equations eq 7 over disordering. Because of this disorder, the real diffusion coefficient used in eq 4 can be much lower than that the one follows from the nearest neighbor hopping rate w.

Our approach is reduced to the analysis of a classical diffusion of an exciton eq 4 with the source and lifetime given by eq 1. Combining both equations together we get

$$\frac{\partial P}{\partial t} = D\frac{\partial^2 P}{\partial \mathbf{r}^2} - rP\left(1 + \frac{{x_0}^3}{x^3}\right) + s(x) = 0 \tag{9}$$

We put the time derivative of the average exciton density equal to zero for the steady state regime, which will be considered in this paper. The organic material is treated as infinite, parallel to the metal surface, so only the x dependence of all parameters is significant:

$$D\frac{d^2P(x)}{dx^2} - rP\left(1 + \frac{{x_0}^3}{x^3}\right) + s(x) = 0 \tag{10}$$

The boundary conditions correspond to the absence of exciton current on both boundaries:

$$\frac{dP}{dx} = 0 \quad x = t_{int}, \quad t_{int} + t_s \tag{11}$$

where t_{int} is the thickness of the intermediate layer separating the emission layer from the metal (see Figure 1b) and t_s is the thickness of the emissive layer. When the metal and the emissive layer are not separated, $t_{int} = 0$.

The emission intensity per unit area is defined by the average rate of photon emission:

$$Y_1 = \int_{t_{int}}^{t_{int}+t_s} rP(x)\,dx \tag{12}$$

The intensity of the radiationless energy transfer is given by

$$Y_2 = \int_{t_{int}}^{t_{int}+t_s} rP(x)\frac{{x_0}^3}{x^3}\,dx \tag{13}$$

The emission efficiency Y is given by the ratio of the emission intensity ($\propto Y_1$) and the total exciton decay $Y_{tot} = Y_1 + Y_2$:

$$Y = \frac{Y_1}{Y_1 + Y_2} \tag{14}$$

This is the main factor defining the quenching effect on device performance.

The diffusion length l_D is given by the distance moved by the exciton during its lifetime $1/r$:

$$l_D = \sqrt{D/r} \tag{15}$$

III. Analysis of Experimental Data and Parameter Dependences for Quenching

To describe electrode quenching, we start with the definition of the exciton diffusion coefficient in the emissive material. We focus on the Alq_3 emissive layer, one of the most efficient light emitting materials for OLEDs. The emission efficiency quenching in Alq_3 due to the energy transfer to the metal has been studied[14] for metal electrodes made of Ca, Ge, and Ag. For all three metals, thick metal coverage of 30 nm of Alq_3 quenches about 70% of the photoemission efficiency. These experimental data permit extraction of the quenching effect.

It is reasonable to assume that for the photoexcited molecules the excitations are distributed uniformly through the Alq_3 sample. Then eq 10 with uniform source can be used:

$$\frac{d^2P(x)}{dx^2} - \frac{1}{{l_D}^2}P\left(1 + \frac{{x_0}^3}{x^3}\right) + \frac{s}{D} = 0 \tag{16}$$

where the exciton diffusion length l_D is defined in eq 15. We consider the silver sample because data related to quenching are available for it.[17,28,29] To describe exciton quenching due to the energy transfer to the metal, we have used the refractive index parameters $n_1 \approx \sqrt{2}$ for Alq_3, $n_2 = 0.06$, and $K_2 = 4.11$ for Ag[27] (see refs 17, 28, and 29) and the resonant wavelength for Alq_3 $\lambda = 528$ nm. Substituting those parameters into eq 2, we get the definition of the effective “quenching thickness” $x_0 = 8.5$ nm in eq 16. The comparison of theory with the experimental data performed in ref 17 for silver induced quenching confirms the x^{-3} dependence, but the minimum proportionality constant is found about 2 times smaller in the experiment.[17,28,29] If we use it, we get $x_0 \approx 6$ nm.

The numerical solution of eq 16 with the boundary conditions eq 14 gives the emission efficiency 30% as in the experiment[14] if we take the diffusion length $l_D \approx 24.7$ nm for theoretically defined quenching length $x_0 \approx 8.5$ nm or $l_D \approx 29$ nm for quenching length $x_0 = 6$ nm defined by the experimental data. This is in reasonable agreement with the crude experimental estimates[14,18] of $l_D \sim 20$ nm.

It is interesting to compare these results with the absorbing wall, an approach which is relevant for extremely strong quenching at the interface only (faster than the diffusion rate), while in the bulk the quenching is negligible. This system can be described by the diffusion equation with the losses due to emission

$$\frac{d^2P}{dx^2} - \frac{P}{{l_D}^2} + \frac{s}{D} = 0 \tag{17}$$

and the boundary condition at the interface with the metal $P(0) = 0$ corresponding to absorption at the wall. The analytical solution of eq 17 yields the emission efficiency

$$Y = 1 - \frac{l_D}{t_s}\tanh\left(\frac{t_s}{l_D}\right) \tag{18}$$

We need to take $l_D \approx 25$ nm to get the experimental value of the emission efficiency 30% for the sample thickness $t_s = 30$ nm. This estimate is close to the results above and the experimental data.[14,18] We have considered the length dependence of the emission efficiency following both approaches to quenching, and the results are shown in Figure 2a for small thicknesses $t_s \leq 7$ nm and in Figure 2b for larger thicknesses. One can see that two mechanisms differ substantially at short distances only, while at longer distances the dependences are almost identical. At short distances the quenching caused by the long-range energy transfer is smaller. It shows ${t_s}^{-3}$ length dependence, while the short-range quenching yields the dependence ${t_s}^{-4}$ for $t_s \ll l_D$ (see eq 18). Since the dependence of emission efficiency on the thickness t_s is not given in ref 14, we cannot reach definite conclusions about the quenching mechanism at the interface of Alq$_3$ with silver. The existing data can be fitted by both models with similar assumptions concerning the diffusion length.

The Al–Alq$_3$ system is very significant for practical purposes because of the stability of the Al cathode in comparison with other active metals.[21] According to theoretical estimate of ref 17, the Al contact should produce relatively weak quenching of excited molecules, comparable to that of silver. However, experimental data for Al[17] yield an almost order of magnitude stronger quenching. If we use the refractive index data for Al $n_2 = 0.43$ and $K_2 = 4.64$ (see refs 17, 28, and 29) in eq 2, we get the effective “quenching thickness” $x_0 = 14$ nm in eq 16. Experimentally observed quenching yields $x_0 = 26$ nm. In Figure 3 we show the length dependence of the emission efficiency for the Al–Alq$_3$ system obtained with the diffusion length $l_D = 24.7$ nm for a uniformly distributed source of excitons with theoretical and experimental values for the “quenching thickness” x_0. If we compare the shape of the graphs for theoretical and experimental quenching rates with the emission intensity length dependence obtained in ref 16 (where ${t_s}^3$ dependence was indeed observed), it is clear that the curve based on the experimental parameters (solid line in Figure 3) is much closer to the shape of the experimental curve, where t^3 dependence of the efficiency on the thickness has been seen up to thickness as

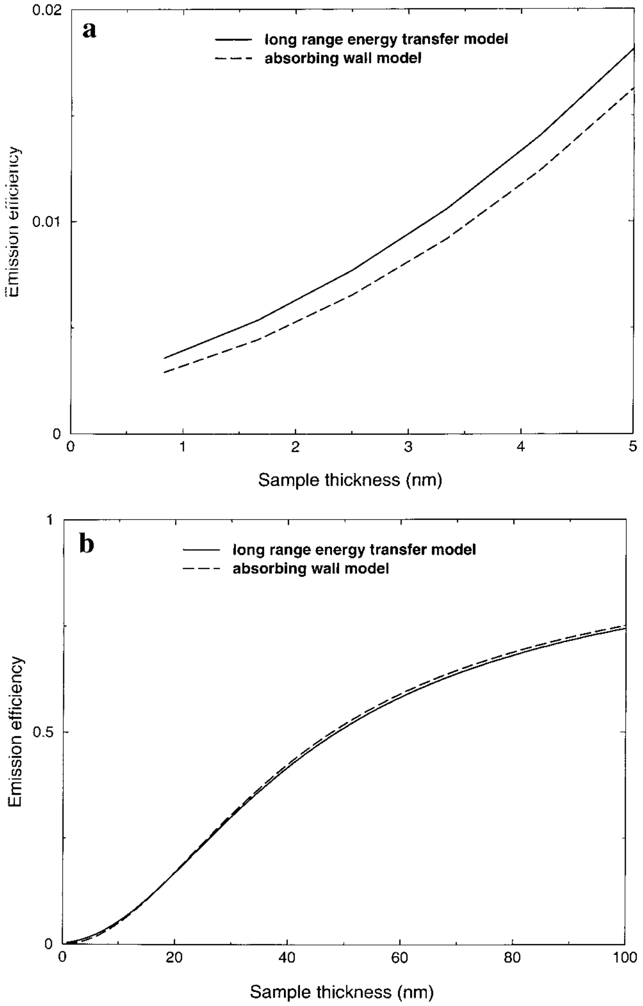

Figure 2. Dependence of the emission efficiency on the Alq$_3$ layer thickness for Alq$_3$–silver system, for small thicknesses (a) and large thicknesses (b), obtained within the framework of the model of long range energy transfer (solid line) or for an absorbing wall (dashed line).

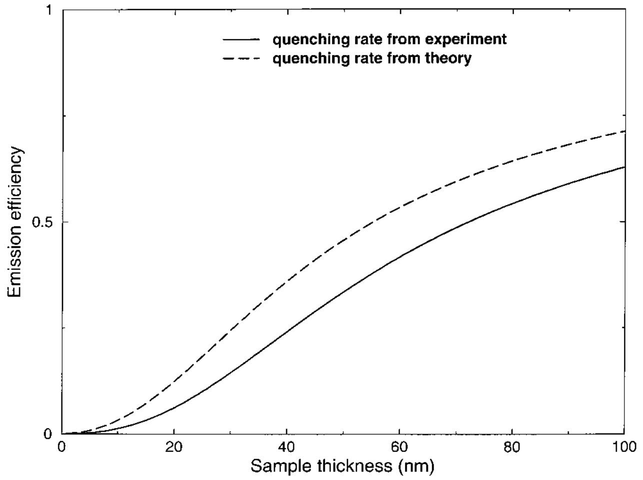

Figure 3. Dependence of the emission efficiency on the emission layer thickness for the Alq$_3$–Al system for the exciton quenching rate calculated theoretically (dashed line) or taken from experiment (solid line).

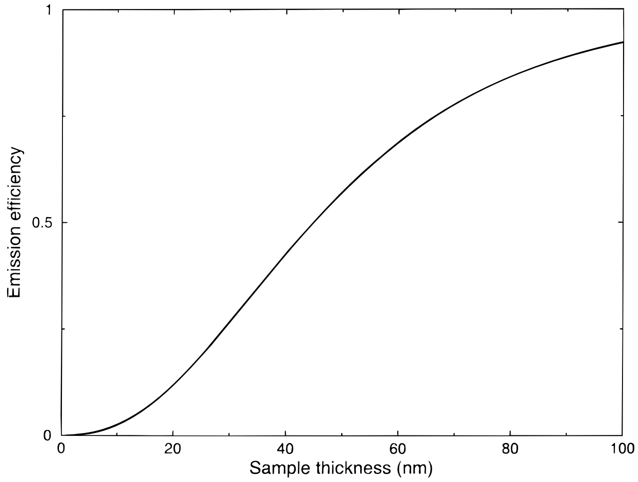

Figure 4. Dependence of the emission efficiency on the emission layer thickness for Alq_3-Al system for the exciton source located near the edge of emissive layer opposite the metal boundary.

large as 50 nm. Therefore we will use the "experimental" length parameter $x_0 = 26$ nm in future calculations for the Alq_3-Al system.

Note that for the Alq_3-Al system the emission efficiency turns out to be significantly lower than that obtained for the absorbing wall model, eq 18. The relevance of that model for Alq_3-Ag can be due to the specially low value of the rate of exciton radiationless decay. At the layer thickness of Alq_3 $t_s = 50$ nm used in OLEDs[8] theory predicts the efficiency 30%. To get efficiency close to unity, the thickness of the layer must be increased by a factor of 4. Actually for the emissive layer thickness 200 nm, theory predicts the emission efficiency to be 80%. This is not efficient because the applied voltage for that thickness will be about 4 times higher than for 50 nm, and extensive self-absorption can occur.

These results are obtained assuming that excitons are created in each molecule with equal probability for photoexcitation. However, when excitons are formed by electrons and holes coming from the different ends of the sample, the formation process might occur mostly at some optimum location. For instance, in bilayer devices holes need to overcome the barrier to enter the emission layer. If there is an electron on the other side of the barrier (negative ion of Alq_3), it is easier for the hole to join that electron and form a neutral excited molecule (exciton) (see, e.g., ref 6). If this channel dominates, then excitons would mostly be formed near the edge of the emissive layer opposite the metal boundary.

To describe this realistic case, one should take the source term in eq 10 in the form

$$s(x) = S\delta(t-x) \tag{19}$$

We have solved eq 10 with this new definition of the source term. The resulting length dependence of the emission efficiency is shown in Figure 4. It is about a factor of 1.5 greater than that for the uniform exciton source (see Figure 3). One can conclude that it is about 50% at $t_s = 50$ nm. To obtain an emission efficiency close to unity, the sample thickness should be increased about twice. In particular it reaches 90% for $t_s \approx 100$ nm.

We cannot decide, based on our calculations, whether the formation of excitons occurs uniformly or near the edge of the emissive layer for the experimental data of ref 16. Comparing the emission efficiency thickness dependence given by the solid line in Figure 3 or 4 with the experimental dependence,[16] we cannot say which line better reproduces the experimental dependence, although Figure 3 looks closer to the experiment. The absolute value of the efficiency or measurements of length dependence up to saturation are necessary to address this question. Irrespective of the domain of exciton formation, we can conclude that at least half to two-thirds of the emission efficiency is lost by quenching, due to the metal interface for 50 nm thickness of the emissive layer. These losses can be lowered by changing the system parameters. We have already considered one way to decrease them by increasing the sample thickness. Another way is to insert an intermediate layer between Al and Alq_3. There are two options for that intermediate layer. It might be an ultrathin dielectric like LiF, which has been used in OLEDs to increase their performance.[9,21] The main effect of this layer is in decreasing the work function of Al leading to strong enhancement of the electron injection,[30] but it also affects the quenching rate. Another option is to insert an additional (organic) electron transport layer between the cathode and the emissive layer.

Consider the effect of a dielectric inorganic layer like LiF. This layer cannot conduct carriers, so its thickness must be very small. Practically it is restricted to 2 nm. LiF has dielectric constant $\epsilon_{nm} \approx 2$,[32-34] almost the same as the dielectric constant of organic materials. The numerical analysis of eq 10 shows that the insertion of the intermediate layer of thickness $t_{int} < 2$ nm with the same dielectric properties as the emissive layer does not affect emission efficiency if the rate of exciton quenching remains the same but the distance to the metal is restricted by the thickness of the layer (note that for this situation the absorbing wall model of eq 18 is inappropriate).

However, when the dielectric constant of inserted layer is greater than that of the emissive layer, the interaction between excited molecule and metal should decrease because of the screening of the electric field of the molecule. The dielectric constant of intermediate layer ϵ_∞ should be taken at high frequency where there are no contributions of vibrational modes. The materials with high electronic dielectric constant are for example GaAs or AlAs having $\epsilon_\infty \sim 10$ (see, e.g., ref 31). Use of these materials as the dielectric layers instead of LiF can suppress metal quenching.

If the organic electron transport layer is inserted between the Al cathode and the Alq_3 emissive layer, it can affect the emission efficiency by restricting the minimum distance from the metal to the emissive layer through which the energy can be transferred. Neglecting the difference in dielectric constant, one can describe the effect of an inserted electron transport layer, placing the lower boundary for exciton diffusion at $x = t_{int}$ where t_{int} is the thickness of the electron transport layer. In Figure 5 we show the emission efficiency depending on the thickness of the intermediate layer. As follows from Figure 5, when the thickness of the electron transport layer reaches 30−40 nm (for the fixed thickness of Alq_3 emissive layer 50 nm) the emission efficiency becomes close to its maximum value 100%.

The exciton diffusion coefficient in Alq_3 can in principle be changed. The lack of understanding the diffusion mechanism does not allow us to give general ways to control the exciton diffusion coefficient. The relevant suggestions involve (but are not restricted to) the addition of impurities which might trap excitons (like quinacridone in ref 19) or changing the extent of disorder, which changes the exciton diffusion. The diffusion length dependence of the emission efficiency is shown in Figure 6. Its sensitivity to the diffusion coefficient is not strong for a uniform source of excitons. Actually, for very low diffusion

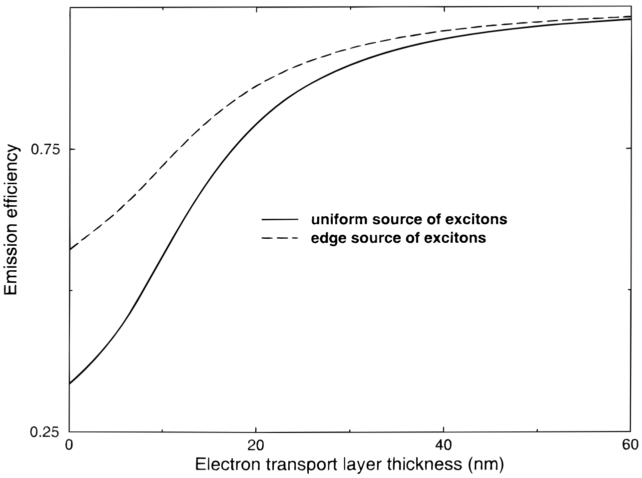

Figure 5. Dependence of the emission efficiency on the thickness of the electron transport layer inserted between cathode and emissive layer for an Al cathode and an Alq_3 emissive layer (solid line for uniform source of excitons and dashed line for exciton source located at the edge of the layer).

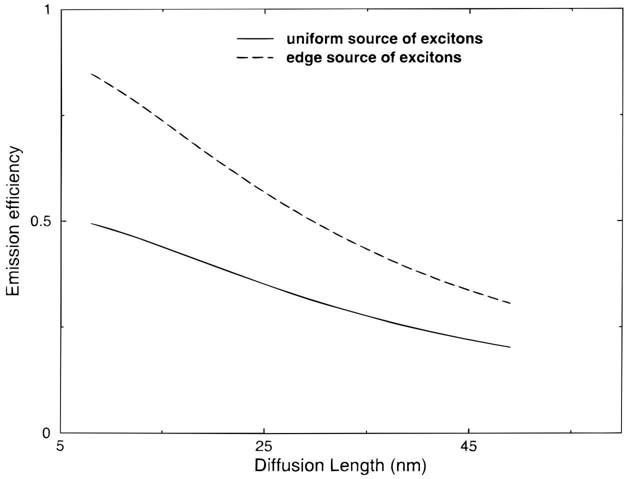

Figure 6. Dependence of the emission efficiency on the diffusion length (solid line for uniform source of excitons and dashed line for exciton source located at the edge of the layer).

coefficient, excitons initially formed close enough to the metal will basically contribute to the radiationless decay, while excitons formed far enough from the metal ($x > x_0$) emit light. The weight of these emitting excitons corresponds to the ratio of the quenching length x_0 and the sample size t_s; close to the saturation value of the efficiency $y \sim 40\%$ at small diffusion lengths (Figure 6). If all excitons are created at the edge of the emissive layer, they cannot migrate close enough to the metal to be quenched if the diffusion coefficient is low enough. When the diffusion length decreases to 10 nm, emission efficiency increases to 80%.

In principle it is possible to use very thin cathodes, several tens of nanometers or even thinner. According to the theory[17] and experiment,[14] we can expect that when the thickness of the cathode becomes smaller than that of the emissive layer the efficiency of quenching would be partially suppressed.

IV. Conclusion

We have studied the quenching effect of the metal boundary in organic light emitting diodes. A model based on classical theory of nonradiative energy transfer to the metal[17] and on a phenomenological model of exciton diffusion has been developed and used to analyze the exciton quenching in Alq_3. We find that the exciton diffusion length is roughly 24.7 nm, which is close to the experimental estimates.

We suggest that a typical OLED using a 50 nm emissive layer of Alq_3 in contact with an Al electrode loses between half and two-thirds of quantum efficiency due to quenching caused by the metal. Ways to suppress quenching and increase emission efficiency by changing various system parameters have been studied.

In particular, increase of the emissive layer thickness would decrease quenching. However, to get meaningful enhancement we must increase the thickness to several hundred nanometers. This can cause several disadvantages, for instance due to self-absorption of emitted light.

Probably the best option is to insert an electron transport layer between the emissive layer and the cathode. According to our estimate the inserted layer of thickness of 30−40 nm can almost completely suppress quenching.

Although the use of ultrathin inorganic dielectric layer with large electronic dielectric constant (like AsGa or AsAl having a dielectric constant $\epsilon_\infty \sim 10$) between the cathode and the emissive layer can strongly suppress quenching, it is not clear whether this material would be as useful as LiF, which has a low dielectric constant but increases the electronic injection rate.

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