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Energy transfer probability in organic electrophosphorescence device with dopant*

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Based on the energy transfer process from host to dopant in an organic electrophosphorescent (EP) device, the expression of energy transfer probability (η) between the host (TPD) and guest ($Ir(ppy)_3$) EP systems was proposed. The results show that: (1) The rate of the triplet energy transfer (K_{HG} and K_{GH}) increases exponentially with increasing donor-acceptor molecular distance (R), whereas decreases as the intermolecular distance (R_{HH}) increases from 0.8 to 2.4 nm. Furthermore, K_{GH} changes more quickly than K_{HG}. (2) The energy transfer probability (η) increases as R reduces, and the R_{HH} changes can be safely neglected for R <0.9 nm. The situation changes for 0.9nm< R < 1.1nm, R_{HH} (< 1nm) plays an essential role when η changes and increases with the latter. However, if R > 1.1nm, the transfer probability will be below zero. Here, the energy transfer principle may be less important, and the high electroluminescence (EL) quantum efficiency of phosphorescent system will be attributed to the direct electron-hole recombination in phosphorescent molecules. (3) The η will increase when the Forster radius (R_0) increases or Gibb's energy decreases.

Keywords: electrophosphorescence, energy transfer, triplet
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1. Introduction

Organic electrophosphorescence (EP) with dopant is of interest due to their ability to harness both triplet and singlet states, leading to organic light-emitting devices (OLEDs) with internal quantum efficiencies of approaching 100%.[1−3] It is a form of electroluminescence (EL) where the optical emission originates from triplet excitons, relaxing radiatively to the ground singlet electronic state (S_H). In contrast to normal LEDs,[4−6] the emission of such LEDs originates from the radiative decay of the triplet states produced by direct electron–hole recombination in phosphorescent molecules or excited by triplet energy transfer from a donor material.[7] Also, energy transfer from the phosphorescent triplets may lead to the excitation of singlet states of another fluorescent dopant material. When the energy acceptor is located at a proper distance, the energy transfer becomes a dominant process.[8] However, a serious problem in maximizing the EL quantum efficiency of phosphorescent LEDs is due to the inefficient energy transfer probability. On the one hand, the energy of the host's excited singlet state falls in triplet states through intersystem crossing (ISC), and forms the long-living triplet states, the triplet host levels will become the "energy reservoir" for the phosphorescent guest triplet (T_G) states and block the transfer from the host material to the guest acceptor. Moreover, they can be easily quenched in the triplet–triplet and / or triplet-charge carrier annihilation processes.[9,10] On the other hand, the excited triplet energy is stored in the host sublattice and can return to acceptor triplets under a proper energetic condition. Triplet dynamics in a guest–host system, i.e. the rates of forward and backward transfer, is determined by the Gibb's energy change and the molecular overlap. In addition, the Forster energy transfer radius (R_0) plays an important role in the energy transfer processes between host-guest singlet states.

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In this paper, we define a formula for energy transfer probability and discuss the energy transfer process between the host–guest phosphorescent systems.

2. Model and formula

Radiative and non-radiative decay processes of electrophosphorescent system are illustrated in Fig.1. The excited singlet (S_H) state of the host molecule has a relatively short lifetime due to the ISC formation (K_H^{ISC}) of host triplets (T_H) and rapid Forster energy transfer (K_{HG}^S) to dopant molecules of guest populating their singlet states (S_G). The guest triplet states (T_G), populated initially by the ISC transition from the excited singlets (S_G) with a rate K_G^{ISC} are complemented with time by the back Dexter transfer from host triplets. The overall radiative and non-radiative monomolecular decay rate constants for excited singlet species are designated respectively by K_H^S and K_G^S. The triplet excitation exchange between host and guest is represented by K_{HG} or K_{GH}. K_H and K_G are respectively the rate constants for the monomolecular decays of triplet state of host and guest.

Corresponding to the scheme in Fig.1, we define the energy transfer probability as

$$\eta = \frac{K_{HG}^S + K_{HG} - K_{GH}}{K_{HG}^S + K_H^S + K_H^{ISC}}, \tag{1}$$

where K_{HG}^S is the Forster energy transfer rate

$$K_{HG}^S = \tau_S^{-1}\left(\frac{R_0}{R}\right)^6. \tag{2}$$

Here, τ_S is the host fluorescence lifetime, R is the molecular distance between donor and acceptor, R_0 is the Forster radius which can be calculated independently by comparing the fluorescence spectrum of the host with the absorption spectrum of the guest. The expected relation is

$$R_0^6 = 8.8 \times 10^{-23} K^2 \phi_D n^{-4} \int_0^\infty F_D(\omega)\varepsilon_A(\omega)\omega^{-4}\mathrm{d}\omega, \tag{3}$$

where K^2 is an orientation factor (2/3 for random orientation), n is the refractive index of the host, ϕ_D is the fluorescence quantum efficiency of the guest, $F_D(\omega)$ is the normalized fluorescent spectrum of the host, $\varepsilon_A(\omega)$ is the molar decadic extinction coefficient of the guest, and ω is the energy in wave number. The mathematic meaning of the formula $\int_0^\infty F_D(\omega)\varepsilon_A(\omega)\omega^{-4}\mathrm{d}\omega$ is the exchange integral of the emission spectrum of donor and the absorption of the acceptor.

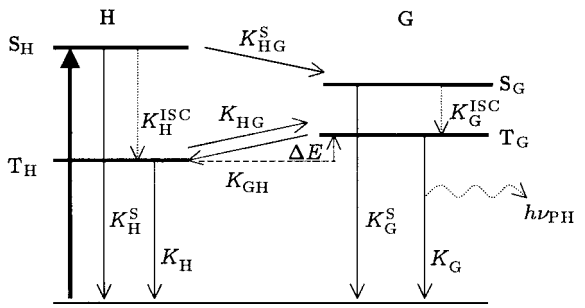


Fig.1. Kinetic scheme illustrating the photophysical processes of electrophosphorescent system.

The triplet energy transfer from host to guess occurs in the Dexter mechanism which is underlain by the short-range electron exchange interaction, and can be expressed in virtue of the following rate constant:[11]

$$K_{GH} = K_G \exp\left[\gamma_{GH}\left(R - \frac{\sqrt{3}}{2}R_{HH}\right)\right], \tag{4}$$

where R_{HH} is the intermolecular distance between the molecules of the host, when molecular cluster formation is neglected, and $\gamma_{GH} = 2/L$ with L being the so-called Bohr radius which characterizes the interaction range (overlap between the electronic orbits of the reactants). The triplet energy transfer from host to guest is impeded by the energy barrier ΔE. Thus,

$$K_{HG} = 4\pi D R \exp(-\Delta E/\kappa T)/R_{GG}^3, \tag{5}$$

where R_{GG} is the average separation between guest molecules.

In contrast to K_{GH} (4), K_{HG} contains the triplet exciton diffusion coefficient,

$$D = \frac{1}{6}\nu_0 R_{HH}^2 \exp(-\gamma_{HH} R_{HH}), \tag{6}$$

where γ_{HH} is a constant representing the distance dependence of the energy coupling between host molecules, and ν_0 is the usual frequency factor with its value in the range of 10^{12}–10^{13} /s^{-1}.

According to the data derived from Ref.[8], we select TPD:Ir(ppy)$_3$ the phosphorescent dopant system, and the molecular structures of Ir(ppy)$_3$ and TPD are shown in Fig.2. The material parameters used in the calculation are listed in Table 1.

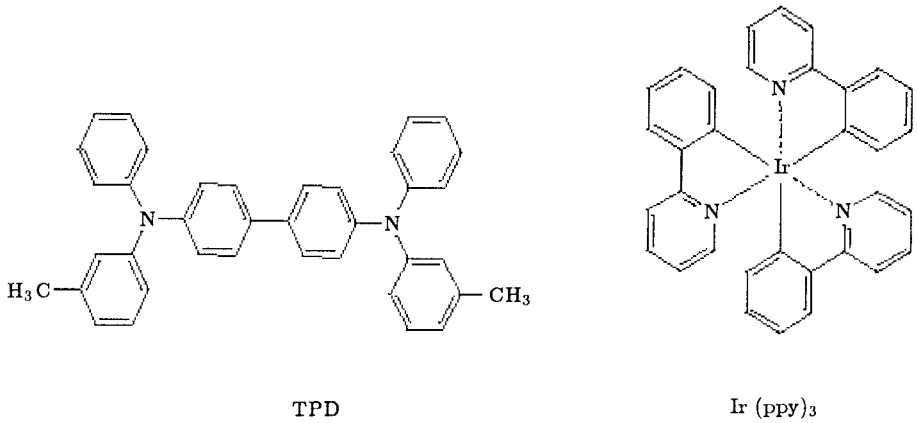


Fig.2. Molecular structures of $Ir(ppy)_3$ and TPD.

Table 1. The parameters used in calculation.

$\gamma_{GH}(2/L_{GH})$/nm	$\gamma_{HH}(2/L_{HH})$/nm	R_{GG}/nm	R_0/nm	$K_H^S(\tau_S^{-1})/s^{-1}$	K_G/s^{-1}	ν_0/s^{-1}	ΔE/eV
17.5	8.5	2.47	1.05	10^9	6.5×10^5	10^{13}	0.1

In the calculation, we assume $K_{HG}^S >> K_H^{ISC}$. This assumption is experimentally underlain due to the lacking fluorescence band ($\approx$ 400nm) of TPD in measured emission spectrum.[12]

3. Results and discussion

The rate constant of the triplet-state energy transfer of the TPD:$Ir(ppy)_3$ phosphorescent dopant system is shown as a function of the intermolecular distance R_{HH} of TPD and the molecular distance R between TPD and $Ir(ppy)_3$, in Fig.3 (a) K_{HG} and (b) K_{GH}. The rate of the triplet energy transfer is an exponential function of R and decreases with R_{HH} increasing from 0.8 to 2.4nm. Furthermore, K_{GH} changes more quickly than K_{HG}. When the molecular distance between the host and guest increases, the triplet–triplet annihilation will occur with a small possibility, which is good for the triplet energy transfer. However, a larger R_{HH} means a higher concentration of guest, which easily leads to the formation of triplet excimers and quenching in guest. The annihilation of the triplet excimers would reduce the rate of energy transfer, whether it is from TPD to $Ir(ppy)_3$, K_{HG}, or inverse K_{GH}. Since the "energy reservoir" is for the phosphorescent $Ir(ppy)_3$ triplet states (T_G) on triplet TPD levels (T_H), K_{GH} is more important than K_{HG} when R or R_{HH} changes.

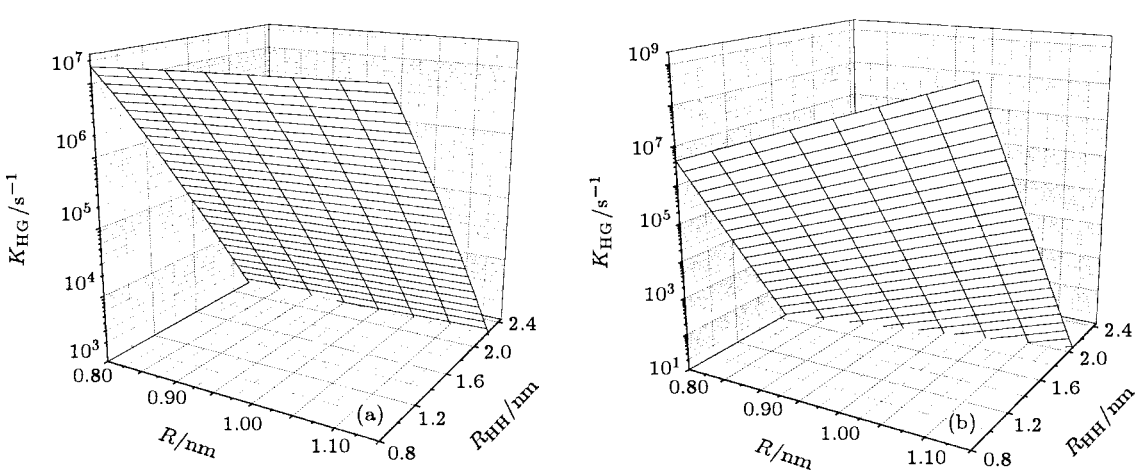


Fig.3. The model of triplet energy transfer from TPD to $Ir(ppy)_3$, K_{GH}, and inverse, K_{GH}, versus TPD-$Ir(ppy)_3$ molecular distance, R, and intermolecular distance, R_{HH}, between molecules of TPD as calculated according to the data given in Table 1.

Figure 4 shows the energy transfer probability (η) versus the molecular distance between the host and guest, R, and the intermolecular distance of the host, R_{HH}. Here, η is reduced with increasing R and can be safely neglected for $R < 0.9$nm when R_{HH} changes. The situation changes for 0.9nm$< R <$ 1.1nm, R_{HH} ($<$ 1nm) plays a central role, when η changes and increases with R_{HH}. However, if $R >$ 1.1nm, the transfer probability will be below zero. Here, the energy transfer principle may be less important. As discussed above, K_{GH} changes more quickly than K_{HG} when R increases. Thus, the total effects make η decrease. As far as the singlet energy transfer is concerned, the Forster energy transfer from host singlet states to guest singlet states, K_{HG}^{S}, falls with increasing R. K_{HG}^{S} will have a larger rate if R becomes smaller, and the effect of R_{HH} on η is comparatively small. However, when R approaches R_0, the Forster energy transfer will not be dominant in η. However, a suitable increase in R_{HH} ($<$ 1.0nm) will affect η significantly, which gives rise to more interactions between TPD and Ir(ppy)$_3$ molecules. If R is large enough to extend the distance for energy transfer, the energy transfer principle may be less important and the high EL quantum efficiency of the phosphorescent system can be attributed to the electron–hole recombination in phosphorescent molecules.

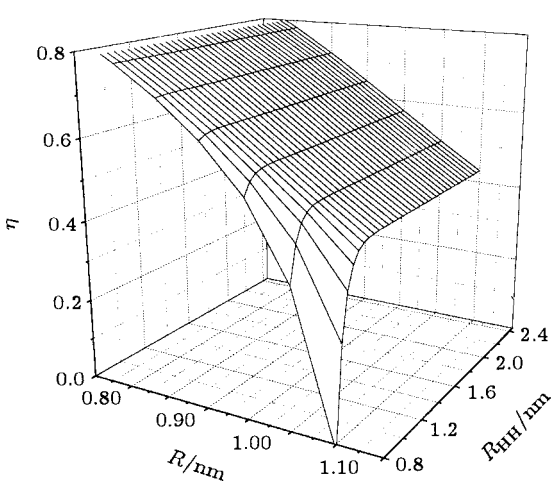


Fig.4. The energy transfer probability (η) versus the distance between TPD-Ir(ppy)$_3$ molecules, R, and the intermolecular distance, R_{HH}, of TPD.

Figure 5 shows the triplet energy transfer ratio $K = K_{HG}/K_{GH}$ of the dopant systems versus Gibb's energy change. It is seen that at R=0.9nm, R_{HH}=1.0nm, K_{HG} increases exponentially for the EP dopant materials as Gibb's energy increases; and if the excited triplet state of the guest is higher than that of the host, good energy transfer between TPD and Ir(ppy)$_3$ will not occur, even if good overlap of host emission and guest absorption occurs (Fig.6). This holds true for charge transfer systems as well, since a lower level in a host could allow energy to be transferred from the excited guest molecule to the host after charge recombination. By designing hosts with a higher first excited triplet state (T_1), the phosphorescent guest will lose less of its energy in a non-radiative way.

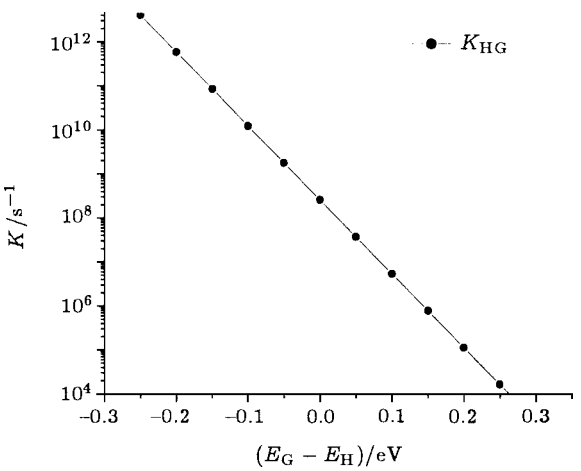


Fig.5. Triplet energy transfer rate from TPD to Ir(ppy)$_3$ versus Gibb's energy change.

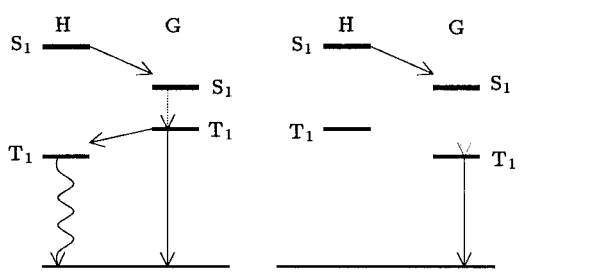


Fig.6. Comparison of guest–host T_1 energy level alignment between suboptimal and optimal guest–host electrophosphorescent systems.

It is noticed that there is an approximately linear exponential dependence of the Forster energy transfer rate, K_{HG}^{S} on Forster radius, R_0, as shown in Fig.7, suggesting that R_0 plays an important role in the increase of η. It can be observed from Eq.(3) that a bigger R_0 would be obtained when the donor has a higher phosphorescent quantum efficiency, the acceptor gains a larger molar decadic extinction coefficient or more overlap areas between the emission spectrum of donor and the absorption of the acceptor, which can make energy transfer efficiently.

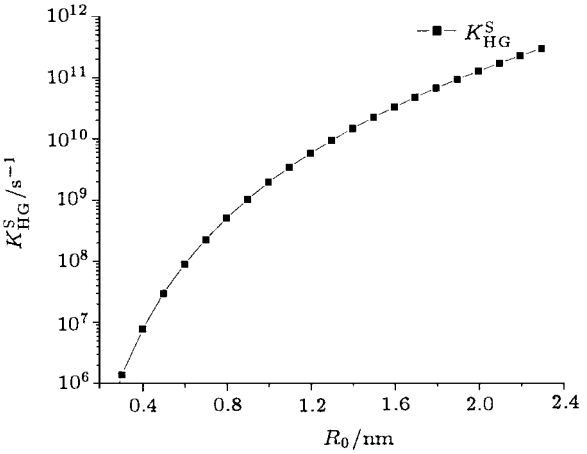


Fig.7. Singlet transfer rate from TPD to $Ir(ppy)_3$, K^{S}_{HG}, versus Forster radius.

4. Conclusion

We have shown that the molecular distance between the host and guest R, and the intermolecule distance of the host R_{HH} in EP dopant system strongly affect both the rate and the probability of the triplet energy transfer. By calculation, we find the rate of the triplet energy (K_{HG} and K_{GH}) increases exponentially with increasing R and decreases with increasing R_{HH}. However, the energy transfer probability (η) increases with decreasing R, and the changes of R_{HH} can be safely neglected for $R < 0.9$nm. For 0.9nm$< R <$ 1.1nm, R_{HH} ($<$ 1nm) plays the central role in η and increases with η. However, if $R > 1.1$nm, the transfer probability will be below zero. Here, the energy transfer principle may be less important, and the high EL quantum efficiency of the phosphorescent system will be attributed to the direct electron-hole recombination in phosphorescent molecules. As defined[8] by $R_{HH} = 10^7 \times (M/c\rho N_A)^{1/3}$ (c is the concentration of the host by weight percent, ρ is the density and M the molecular weight of host, and N_A is Avogadro's number). Actually, R_{HH} reflects the dopant concentration in the host. The higher the concentration, the smaller the R_{HH} will be. We also show that the triplet energy transfer ratio K of the dopant systems versus Gibb's energy change $E_G - E_H$ and the dependence of the Forster energy transfer rate K^{S}_{HG} on Forster radius R_0, moreover $E_G - E_H$ and R_0 have great effect on η also. As a result, in the processes of optimizing EP devices, the above factors should be considered seriously.

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