Energy Transfer Probability Between Host and Guest in Doped Organic Electrophosphorescent Devices [*]

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Abstract: An expression for energy transfer probability ( ) between host (TPD) and guest (Ir(ppy)$_3$) phosphorescent systems is proposed, and the energy transfer process in doped organic electrophosphorescent (EP) devices is discussed. The results show that (1) The rate of the triplet energy transfer (K_{HG} and K_{GH}) exponentially increases with the host-guest molecular distance (R), and K_{HG} decreases quickly as the intermolecular distance of the guest (R_{GG}) increases. In addition, the K_{HG}/K_{GH} ratio of the dopant system increases when R or R_{GG} is reduced; (2) The energy transfer probability approximately linearly decreases as R increases from 0.8 to 1.2nm, and the variation of R_{GG} can be neglected when R < 1.1nm. For 1.1nm < R < 1.2nm, R_{GG} (< 1.6nm) plays an increasingly important role when drops with the latter; (3) increases when the Forster energy transfer rate increases or Gibb's energy declines.

1 Introduction

Molecularly doped host-guest (H-G) phosphorescent blends have recently been exploited to facilitate the understanding of the physics of organic materials and improve the efficiency of organic-emitting devices (OLEDs)[1,2]. These attributes result from the phosphorescent molecule's harnessing of both triplet and singlet states, leading to OLEDs with internal quantum efficiencies approaching 100%[3,4]. The doped phosphorescent guest emission usually originates from the triplet energy transfer in the donor material[5]. Furthermore, the energy transfer rate depends on the intermolecular distance of the guests and the molecular distance between the host and guest doped systems. When the energy acceptor is located at a proper distance, the energy transfer dominates in the process[6]. However, a serious problem in maximizing the EL quantum efficiency of phosphorescent LEDs is an inefficient energy transfer proba-

bility: (1) The energy of the host excited singlet state falls in triplet states through intersystem crossing (ICS), forming long-living triplet states, which block transfer from the host material to the guest acceptor. Moreover, they can be easily quenched in triplet-triplet or triplet-charge carrier annihilation processes[7,8]. (2) The excited triplet energy is stored in the host sublattice and can be returned to the acceptor triplets under a proper energetic condition. (3) Triplet dynamics in a guest-host system: the forward and back transfer rates are determined by the variation of the Gibb's energy and the overlapping of the molecules. In addition, the Forster energy transfer plays a central role in the energy transfer process between the host-guest singlet states. To study the energy transfer mechanism between host and guest in the doped organic electrophosphorescent devices, we define an expression of energy transfer probability and discuss the energy transfer process based on the TPD   Ir(ppy)3 phosphorescent doped system.

2   Model and formula

The radiative and non-radiative decay processes of the electrophosphorescent system are shown in Fig. 1. The excited molecules of the host (S_H) have 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 doped molecules of guests populating their singlet states (S_G). The
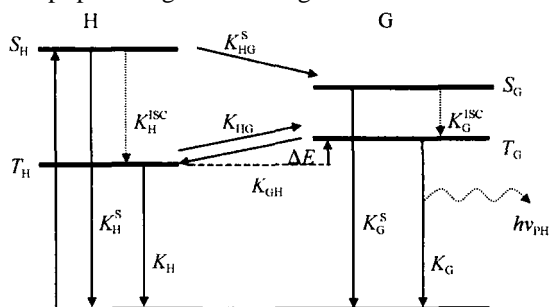

Fig. 1   Kinetic scheme of photophysical processes in the electrophosphorescent system

guest triplet states (T_G), populated initially by the ISC 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 singlet excited species are determined by K_H^S and K_G^S. The triplet excitation exchanges between host (H) and guest (G) are represented by K_{HG} and K_{GH}, respectively. K_H and K_G are the respective rate constants for the monomolecular decay of the triplet state of the host and guest.

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

$$\eta = \frac{K_{HG}^S + K_{HG} - K_{GH}}{K_{HG}^S + K_H^S + K_H^{ISC}} \qquad (1)$$

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

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

Here, τ_s is the host fluorescence lifetime, R is the donor-acceptor molecular distance, and R_0 is the Forster radius, which can be independently obtained by the fluorescence spectrum of the host and the absorption spectrum of the guest. The expected relation is

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

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, $F_D(\nu)$ is the normalized fluorescent spectrum of the host, $\varepsilon_A(\nu)$ is the molar decadic extinction coefficient spectrum of the guest, and ν is the energy in wave number. The mathematical meaning of the formula $\int_0 F_D(\nu) \varepsilon_A(\nu) \nu^{-4} d\nu$ is the exchange integral of the emission spectrum of the donor and the absorption of the acceptor.

The one triplet energy transfer from the host occurs by the Dexter mechanism, which is underlain by the short-range electron exchange interaction, and can be expressed by the rate constant[9]:

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

where R_{HH} is the intermolecular distance between the molecules of the host without consideration the formation of the molecular clusters, and $\gamma_{GH} = 2/L$, where L is the Bohr radius, which characterizes the interaction range (overlapping between the electronic orbits of the reactants). The triplet energy transfer from host to guest is impeded by the energy barrier ΔE. Thus,

$$K_{HG} = 4\pi D R \exp(-\Delta E/kT)/R_{GG}^3 \qquad (5)$$

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

Unlike K_{GH} in Eq. (4), K_{HG} contains the triplet exciton diffusion coefficient,

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

where γ_{HH} is a constant that scales the distance dependence of the energy coupling between host molecules, and ν_0 is the usual frequency factor falling in the range of 10^{12} – $10^{13} s^{-1}$.

According to the data derived from Ref. [5], we select a very efficiently doped system based on an excitation energy donor, a diamine derivative N, N'-diphenyl-N, N'-bis (3-methylphenyl)-1, 1'-biphenyl-4, 4'-diamine (TPD), and an efficient phosphorescent complex fac tris(2-phenylpyridine) iridium [Ir(ppy)$_3$] used in high-efficiency electrophosphorescent systems. The triplet energy transfer between these molecules is subject to modification by the variation in their relative concentrations in a bisphenol A polycarbonate (PC) matrix. The material parameters used in the calculation are listed in Table 1.

Table 1   Parameters used in calculation

$_{GH}$(2/ L $_{GH}$) / nm	$_{HH}$(2/ L $_{HH}$) / nm	R_{HH} / nm	R_0 / nm	K_H^S ($_S^{-1}$) / s^{-1}	K_G / s^{-1}	$_0$ / s^{-1}	E / eV
17. 5	8. 5	1. 0	1. 05	10^9	6.5×10^5	10^{13}	0. 1

In the calculation, we assumed $K_{HG}^S \gg K_H^{ISC}$, which is experimentally underlain by the lack of fluorescence band (400nm) in TPD in measured emission spectrum[10].

3   Results and discussion

For a device with an electrophosphorescent dopant system, the triplet state energy transfer rate constant in the TPD Ir (ppy)₃ phosphorescent dopant system as functions of the intermolecular distance of Ir (ppy)₃, R_{GG}, and the molecular distance between TPD and Ir(ppy)₃, R, are shown in Fig. 2. K_{HG} is exponential proportional to R and decreases with increasing R_{GG}. Moreover, the change of R_{GG} dominates the transfer rate. When the molecular distance between host and guest increases, the occurrence of triplet-triplet annihilation is less probable, benefiting the triplet energy transfer. As defined[5] by $R_{GG} = 10^7 \times (M/c\, N_A)^{1/3}$ (c is the concentration of guest by weight, is the density, M is the molecular weight of the guest, and N_A is the Avogadro's number). A bigger R_{GG} means a smaller doping concentration of the guest. Therefore, if R_{GG} decreases, there is less molecular Ir(ppy)₃ that is surrounded by molecular TPD. The decreased chance for them to interact reduces the energy transfer rate from TPD to Ir(ppy)₃.

There is a linearly exponential dependence in the Forster energy rate (K_{HG}^S) and triplet energy transfer rate (K_{GH}) on the molecular distance R, as shown in Fig. 3. It can be observed from Eq. (3) that a bigger R will make K_{HG}^S decrease. However, T-T annihilation occurs at a lesser probability when the molecular distance of host-guest rises. This is good for the energy transfer from guest triplet to host triplet.

The triplet energy transfer ratio K_{HG}/ K_{GH} in the dopant system versus the host-guest molecular distance, R, and the intermolecular distance of guests, R_{GG}, are analyzed and shown in Fig. 4. Here K_{HG}/ K_{GH} increases as R or R_{GG} drops. As discussed above, there is a slight increase as R rises, resulting in a tremendous decrease in K_{GH}. The triplet energy transfer rate shows a different change direction
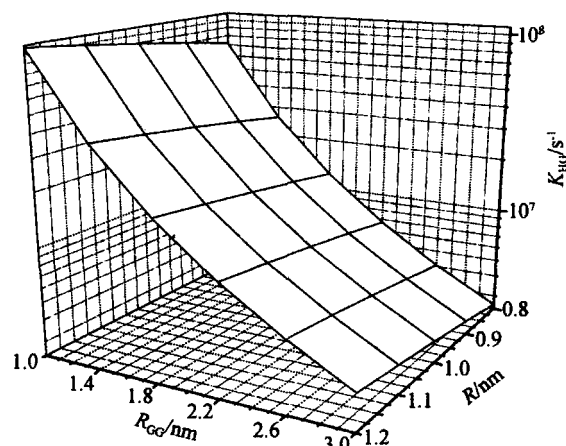

Fig. 2   Model of triplet energy transfer from TPD to Ir(ppy)₃, K_{HG}, versus intermolecular distance of Ir(ppy)₃, R_{GG}, and TPD- Ir(ppy)₃ molecular dstance, R, as calculated according to the data given in Table 1
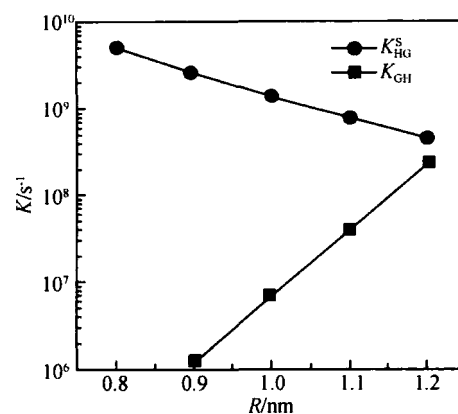

Fig. 3   Triplet energy transfer from Ir(ppy)₃ to TPD, K_{GH}, and Forster energy transfer, K_{HG}^S, versus R, moleculars distance for TPD- Ir(ppy)₃

in when the intermolecular distance of Ir(ppy)₃ increases. Triplet energy transfer from TPD to Ir(ppy)₃, K_{HG}, falls with increasing R_{GG}, while the change of R_{GG} contributes little to the triplet energy rate of K_{GH}. Therefore, K_{HG}/ K_{GH} safely drops as R_{GG} increases from 1. 0 to 3. 0nm.

Figure 5 shows the energy transfer probability ( ) from TPD to Ir(ppy)₃ versus the host-guest molecular distance, R, and the intermolecular distance of guests, R_{GG}. It is seen that   increases linearly when R is reduced from 0. 8 to 1. 2nm, and changes in R_{GG} can be neglected for $R <$ 1. 1nm. The situation changed for 1. 1nm $< R <$ 1. 2nm. R_{GG} plays an increasingly important role when changes and decreases with the latter. The effects are obvious when $R_{GG} <$ 1. 6nm. K_{HG} declines with in-
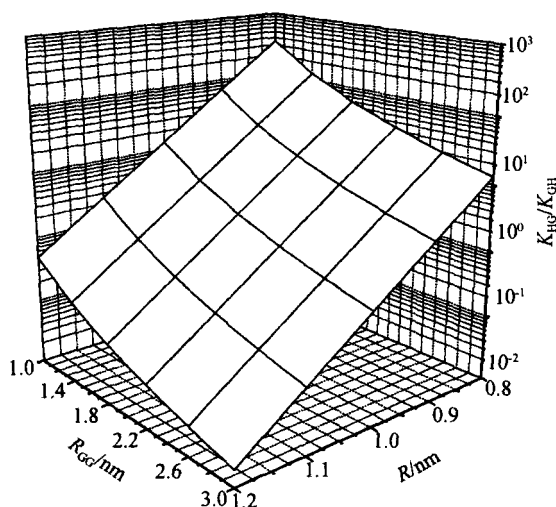
Fig. 4   Triplet energy transfer ratio K_{HG}/ K_{GH} of the dopant system versus TPD-Ir（ppy）$_3$ molecular distance, R, and R_{GG}, the intermolecular distance of Ir（ppy）$_3$
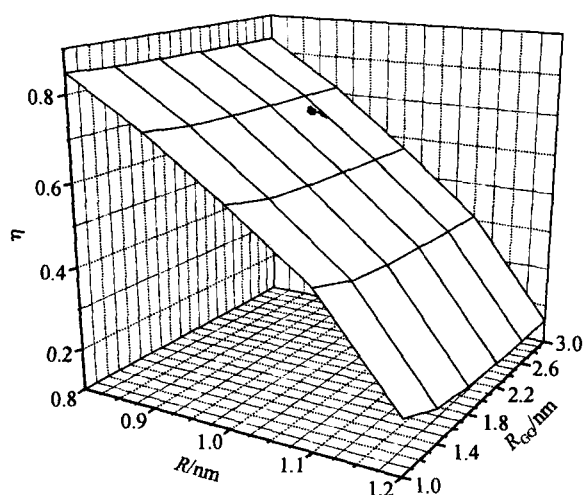

Fig. 5   Relation of the energy transfer probability（ ）versus TPD-Ir（ppy）$_3$ molecular distance, R, and intermolecular distance, R_{GG}, of Ir（ppy）$_3$

creasing R_{GG}. Compared with the contribution from R, K_{HG} can be neglected, especially with a longer guest intermolecular distance. A bigger R_{GG} means a small doping concentration into the guests, and then the energy transfer probability is determined by the Forster energy transfer rate in a singlet state from TPD to Ir（ppy）$_3$. However, if R_{GG} decreases, the energy transfer of the host-guest triplet system may greatly affect . Thus, a

smaller R_{GG} is good for . A similar trend is observed from Fig. 4, in which K_{HG}/ K_{GH} drops as R or R_{GG} increases.

Figure 6 shows K_{HG} at $R = 0.9$nm, $R_{GG} = 2.47$nm, which exponentially increases with increasing Gibb's energy. If the excited triplet state of the guest is higher than that of the host, a good energy transfer will not occur, even with a good overlapping of host emission and guest absorption. This holds true for charge transfer systems as well, since a lower level in the 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 energy through non-radiation.
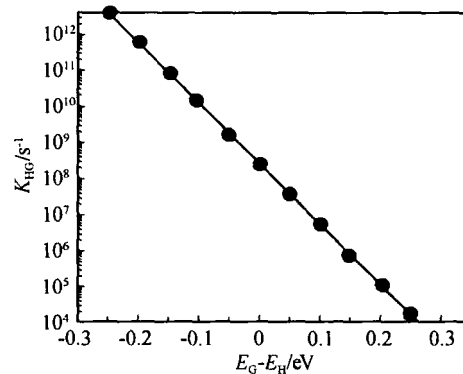

Fig. 6   Triplet energy transfer rate from TPD to Ir（ppy）$_3$ versus Gibb's energy change

4   Conclusion

The dependence of the energy transfer rate and probability on the molecular distance between host and guest, R, and the guest intermolecular distance R_{GG}, are numerically investigated. The following conclusions are obtained: (1) The triplet energy rate（K_{HG} and K_{GH}）exponentially increases with increasing R. However, K_{HG} and K_{GH} have opposite trends when R_{GG} increases; (2) The energy transfer probability（ ）and the ratio K_{HG}/ K_{GH} decrease when R or R_{GG} rises. If $R < 1.1$nm, a smaller R_{GG} plays a central role in ; (3) Gibb's energy change and the Forster energy have strong effects on . In the processes of optimizing EP devices, the above factors should be considered carefully.

References

[1] Thoms T ,Okada S ,Chen J P ,et al. Improved host material design for phosphorescent guest-host systems. Thin Solid Films ,2003 ,436 :264

[2] Chen K O ,Shinar J. Forster energy transfer in combinatorial arrays of selective doped organic light-emitting devices. Appl Phys Lett ,2004 ,84 :1201

[3] Adachi C ,Baldo M A , Thompson E M ,et al. Nearly 100 % internal phosphorescence efficiency in an organic light emitting device. Appl Phys ,2001 ,90 :5048

[4] Li F , Zhang M , Cheng G , et al. Highly efficient electrophosphorescence devices based on rhenium complexes. Appl Phys Lett ,2004 ,84 :148

[5] Baldo M A ,Forrest S R. Transient analysis of organic electrophosphorescence I :transient analysis of triplet energy transfer. Phys Rev B ,2000 ,62 :10958

[6] Kalinowski J ,Stampor W ,Cocchi M ,et al. Triplet energy exchange between fluorescent and phosphorescent organic molecules in a solid state matrix. Chem Phys , 2004 ,297 :39

[7] Baldo M A ,Adachi C ,Forrest S R. Transient analysis of organic electrophosphorescence :transient analysis of triplet-triplet annihilation. Phys Rev B ,2000 ,62 :10967

[8] Kalinowski J ,Stampor W ,Cocchi M ,et al. Quenching effects in organic electrophosphorescence. Phys Rev B , 2002 , 66 : 235321

[9] Klöffer W. Electronic properties of polymers. New York :Wiley ,1982

[10] Kalinowski J ,Cocchi M , Giro G ,et al. Injection-controlled electroluminescence in organic light-emitting diodes based on molecularly-doped polymers : single-layer devices. J Phys D :Appl Phys ,2001 ,34 :2274

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:   (TPD)   (Ir (ppy) $_3$)   ,
.   : (1)   (K_{HG} , K_{GH}) R , K_{HG}
R_{GG} , K_{HG}/ K_{GH} R R_{GG} ; (2) R 0. 8 1. 2nm ,
, $R < 1. 1nm$, R_{GG} , 1. 1nm $< R < 1. 2nm$, R_{GG} ($< 1. 6nm$)
; (3) Forster   Gibb's   ,   .

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