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**Citation:** Zhu, Tianyu, and Troy Van Voorhis. "Unraveling the Fate of Host Excitons in Host–Guest Phosphorescent Organic Light-Emitting Diodes." *Journal of Physical Chemistry C* 123, 16 (April 2019): 10167–702 doi 10.1021/ACS.JPCC.9B02820 ©2019 Author(s)

**As Published:** 10.1021/ACS.JPCC.9B02820

**Publisher:** American Chemical Society (ACS)

**Persistent URL:** <https://hdl.handle.net/1721.1/129452>

**Version:** Author's final manuscript: final author's manuscript post peer review, without publisher's formatting or copy editing

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# Unraveling the Fate of Host Excitons in Host-Guest Phosphorescent Organic Light-Emitting Diodes

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## Abstract

Understanding energy and charge transfer mechanisms in host-guest systems is crucial for improving performance of organic light-emitting diodes (OLEDs), but it presents a theoretical challenge due to disordered molecular environment. Here, we address the fate of excitons that form on the host in a BTDF-Ir(ppy)<sub>3</sub> phosphorescent OLED through a QM/MM simulation. Our results demonstrate that triplet host excitons can be harvested through efficient energy transfer to the T<sub>1</sub> state of the guest allowed by excellent spectral overlap. Detailed analysis of the guest absorption spectrum uncovers that high-lying guest singlet states play a critical role in utilizing singlet host excitons. Furthermore, we investigate the process where host excitons break up and reform on the guest, and show it is unfavored owing to the high energy barrier. This work thus reveals energy transfer is the primary quenching mechanism for host excitons and highlights strategies for better host-guest design.

## Introduction

Organic light-emitting diodes (OLEDs) have been attracting much attention due to their great potential as displays in electronic devices and lighting sources.<sup>1-3</sup> Among various types of OLEDs, phosphorescent OLEDs (PhOLEDs)<sup>4,5</sup> and recently-developed thermally activated delayed fluorescence (TADF) OLEDs<sup>6-9</sup> are most promising because they can harvest both singlet and triplet excitons and achieve 100% internal quantum efficiency.<sup>10,11</sup> No matter what kind of emitter is adopted, the host-guest system is necessary in OLED devices to achieve high external quantum efficiency (EQE). In host-guest systems, emitters (guests) are dispersed homogeneously into host materials in order to minimize triplet-triplet annihilation and exciton quenching.<sup>12,13</sup> As shown by numerous experiments,<sup>14-16</sup> the electroluminescence efficiency of OLEDs is affected significantly by different choices of host-guest combinations because guest exciton formation relies on efficient charge and energy transfers from the host. A recent theoretical study of TADF host-guest systems<sup>17</sup> reveals that static energetic disor-

der for both guests and hosts is determined by the polarity of host molecules. The amount of static disorder affects charge-transport properties and exciton formation pathways, which consequently influence the overall efficiency of an OLED device. Other important properties, such as the color purity<sup>18</sup> and exciton lifetime<sup>19</sup> in OLED devices, also rely on tailored host-guest design. Therefore, understanding host-guest interactions and how they affect energy and charge transfers is crucial for improving performance of OLED devices.

However, the mechanism of guest exciton formation in host-guest systems is not well understood and generally two hypotheses have been proposed.<sup>20,21</sup> First, the holes and electrons recombine primarily on the host, and then the excitation energy is transferred from the host to the guest. This process happens through Förster resonance energy transfer (FRET)<sup>22</sup> for singlet excitons and Dexter energy transfer (DET)<sup>23</sup> for both singlet and triplet excitons. Several new design strategies based on this mechanism are suggested, such as introducing triplet sensitizers,<sup>24</sup> exciplex<sup>25</sup> or TADF molecules<sup>26</sup> to assist energy transfer to the emitters. Second, several other studies reported that charge trapping at guest molecules is the main cause for guest exciton formation.<sup>27,28</sup> This mechanism assumes the guest can capture a charge carrier as a trap site. Such charge carrier can then recombine with a charge carrier of opposite sign to form an exciton.

As host materials typically account for over 90 wt% in an OLED emission layer, even if some guests may trap charge and form excitons directly, effective quenching of host excitons is still necessary to avoid host emission.<sup>5</sup> Moreover, efficient utilization of host excitons for guest emission is crucial for achieving high quantum efficiency. Therefore, understanding how host excitons are quenched is of great importance for better OLED host-guest design.

In this article, we present a theoretical investigation on the fate of excitons that form on the host in a host-guest PhOLED device. The highly-efficient green phosphorescent emitter tris(2-phenylpyridine)iridium ( $\text{Ir(ppy)}_3$ )<sup>5</sup> and 2,8-bis(triphenylsilyl)dibenzofuran (BTDF) are chosen as the guest and host in this study, see Figure 1a.  $\text{Ir(ppy)}_3$  utilizes both singlet and triplet excitons for phosphorescence emission from its  $T_1$  state owing to strong spin-orbit

coupling. BTDF is an electron-conducting host designed for hole-conducting deep-blue emitters.<sup>29</sup> A number of computational studies have been done on the morphology and charge transport properties of BTDF-hosted PhOLEDs on various length scales.<sup>30,31</sup> Recently we have studied the charge recombination mechanism in this BTDF-Ir(ppy)<sub>3</sub> PhOLED using a quantum mechanics/molecular mechanics (QM/MM) method.<sup>32</sup> We found a charge trapping route existing in this system for direct exciton formation on the guest. However, it is still puzzling how host excitons are utilized for guest emission in this system.

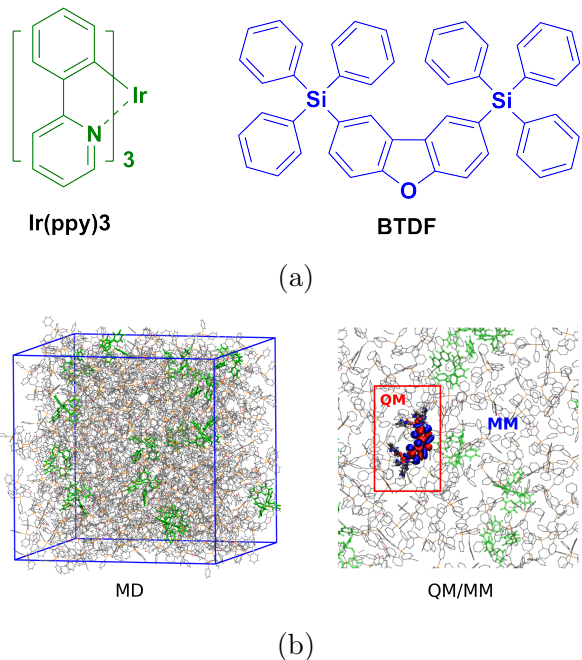


Figure 1: (a) Chemical structures of Ir(ppy)<sub>3</sub> and BTDF. (b) Illustration of MD and QM/MM simulations for BTDF-Ir(ppy)<sub>3</sub> host-guest system. Ir(ppy)<sub>3</sub> (guest) is highlighted in green. Left panel: MD simulation box. Right panel: QM/MM simulation.

While several theoretical methods exist for treating charge transfer problems in molecular materials,<sup>33,34</sup> we use a combined molecular dynamics (MD) and quantum mechanics/molecular mechanics (QM/MM) approach<sup>35</sup> (see Figure 1b). Although the QM/MM method has been extensively employed to investigate molecular materials such as organic photovoltaics,<sup>36–38</sup> it has only been applied to study a few OLED systems by far.<sup>17,32,39</sup> Using the QM/MM approach allows us to sample both spatial and time distributions of guest and host energetics in the emission layer, where conformational fluctuations may have a

significant impact.<sup>40</sup> Meanwhile, our method take the polarizable organic semiconductor environment into account apart from the electrostatic effects, by introducing fictitious “drude” charges.<sup>41</sup> We want to point out that quantum nuclear effect is ignored in our simulation, which may have an impact on exciton diffusion and long-range energy transfer.<sup>42</sup>

We are particularly interested in examining two mechanisms for harvesting host excitons for guest emission: (1) direct energy transfer from the excited host to the guest; (2) indirect charge transfer where host excitons first break up and then reform on the guest. We find that direct energy transfer is the primary quenching mechanism for host excitons, while the charge transfer mechanism is unfavored because of the high energy barrier for exciton dissociation. Our results reveal that triplet host excitons are utilized through efficient Dexter energy transfer, and high-lying excited states of the guest plays an important role in utilizing singlet host excitons. Based on these results, we provide suggestions for rational design of good host and guest combinations in OLED devices.

## Computational Methods

To sample amorphous host-guest structure, we perform an MD simulation in NPT ensemble using the OPLS force field<sup>29,43</sup> in a simulation box containing 15 Ir(ppy)<sub>3</sub> and 250 BTDF molecules. We anneal the system from 0 K to 500 K during 2 ns and then simulate the system at 500 K in an NPT ensemble for another 2 ns to make sure the equilibrium density is reached. The host-guest system is equilibrated at the high temperature (500 K) so that the molecules become spatially uncorrelated and well-sampled amorphous structures can be obtained. The system is then cooled to the room temperature (300K) during 1 ns, after which a 3 ns simulation in NPT ensemble at 300 K is performed. The final 2 ns of the NPT dynamics is sampled at 0.2 ns intervals to obtain 10 snapshots for QM/MM calculations. All MD simulations are carried out using GROMACS 4.5.5 package.<sup>44</sup>

Polarizable QM/MM (QM/MMpol) calculations are then done on the ground and excited

states of the host (75 molecules in 2 MD snapshots) and guest (15 molecules in 10 MD snapshots) using the CHARMM<sup>45</sup>-QChem<sup>46</sup> interface.<sup>47</sup> For each QM/MM calculation, only one guest or host molecule is selected as the QM region, while all other molecules are computed by MM. The fictitious drude charges<sup>41</sup> are introduced to take the polarizable environment into account, where drude charge parameters are fitted to reproduce the polarizability of the host and guest molecules.

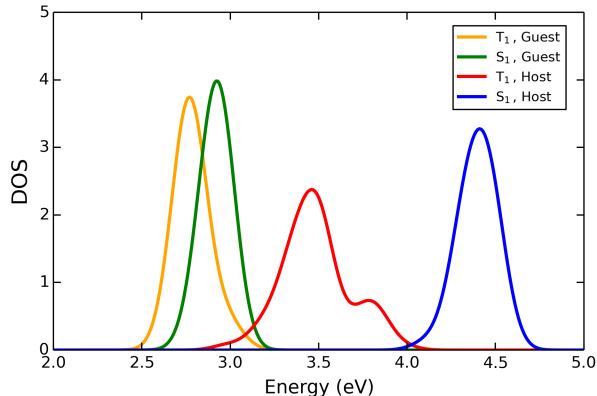
Density functional theory (DFT) is used to compute the QM region with PBE0 functional<sup>48</sup> and 6-31G\* basis set<sup>49</sup> for BTDF and LANL2DZ basis set<sup>50</sup> for Ir(ppy)<sub>3</sub>. Unless specified, unrestricted DFT (UDFT) and a restricted open-shell Kohn-Sham (ROKS) method<sup>51</sup> are employed to compute the T<sub>1</sub> and S<sub>1</sub> states respectively. ROKS calculates the lowest singlet excited state (S<sub>1</sub>) energy by optimizing the KS orbitals to minimize a linear combination of single-determinant energies. This UDFT/ROKS scheme has been shown to provide accurate prediction of charge-transfer excited-state energies for OLED molecules.<sup>52</sup> To further confirm UDFT/ROKS is suitable for our system, we compared it with time-dependent DFT (TDDFT) for gas-phase Ir(ppy)<sub>3</sub> and BTDF using PBE0, B3LYP<sup>53</sup> and  $\omega$ PBE<sup>54</sup> functionals. We find that the excitation energy differences between Ir(ppy)<sub>3</sub> and BTDF computed by UDFT/ROKS with PBE0 are in good agreement with other tested methods (Supporting Information). Thus, this scheme is sufficient for us to obtain useful insights. TDDFT is adopted to compute the full absorption spectrum of Ir(ppy)<sub>3</sub> in the range of 2.5 to 4.5 eV.

## Results

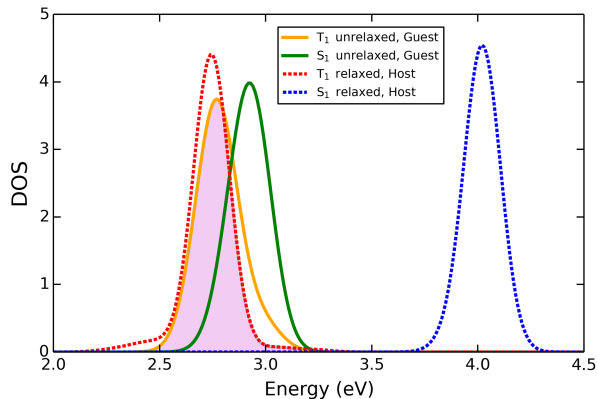
### Energy transfer mechanism

The lowest excited-state energies at MD-sampled ground-state geometries are calculated first (Figure 2a), to which we will refer as unrelaxed exciton energies. These QM/MMpol excited-state energies (150 data points for each state) are then used to construct probability

distributions by applying a kernel density estimation (KDE).<sup>55</sup> Oscillator strengths are not considered in Figure 2 as  $T_1$  states are dark, making this figure a density of states (DOS) plot. As seen in Figure 2a, the unrelaxed  $T_1$  and  $S_1$  energies of BTDF are higher than those of  $\text{Ir(ppy)}_3$  as expected, which guarantees that guest excitons would not transfer energy back to the host.



(a)



(b)

Figure 2: (a) Simulated DOS distributions for unrelaxed  $T_1$  and  $S_1$  excitons on the host and guest. (b) The DOS distributions for relaxed excitons on the host compared to the DOS distributions for unrelaxed excitons on the guest.

To investigate the energy transfer mechanism from excited host to the guest, we then simulate  $T_1$  and  $S_1$  energies of BTDF at its optimized excited-state geometries (Figure 2b), to which we will refer as relaxed exciton energies. Note that the unrelaxed/relaxed  $S_1$  exciton energy is equivalent to the  $S_1$  vertical absorption/emission energy. As MD simulation



only samples ground-state structures, the excited-state geometry optimization is further performed for the host within the non-polarizable QM/MM (QM/MMnonpol) framework where drude charges are turned off. To reduce the computational cost, we freeze geometries of all MM molecules and only optimize the geometry of the selected host molecule in the  $T_1$  or  $S_1$  state. QM/MMpol calculations are then carried out on the optimized excited-state geometries to obtain relaxed exciton energies of the host.

Since 75% of excitons generated from electron-hole recombinations are triplet,<sup>56</sup> it is important to harvest triplet host excitons to achieve high electroluminescence efficiency. Note that it is difficult to measure triplet exciton energies of BTDF in experiments as its triplet state is a dark state. Thus we discuss the triplet energy transfer first. In particular, only Dexter energy transfer (DET) is possible here, whose rate can be expressed as:<sup>23</sup>

$$k_{DET} \propto \bar{J} \exp(-2R_{DA}/L), \quad (1)$$

where  $R_{DA}$  is the distance between donor (D) and acceptor (A),  $L$  is the sum of van der Waals radius.  $\bar{J}$  is the normalized spectral overlap that is proportional to the overlap between DOS of donating and accepting states. It is demonstrated in Figure 2b that the DOS of relaxed  $T_1$  excitons of BTDF overlaps substantially with the DOS of unrelaxed  $T_1$  excitons of Ir(ppy)<sub>3</sub>. This clearly suggests that triplet host excitons are allowed to transfer the excitation energy efficiently to the guest because the DET rate is proportional to the normalized spectral overlap  $\bar{J}$ . The DET rate is also affected significantly by the electronic coupling between donor and acceptor, indicated by its exponential relationship to  $R_{DA}/L$ . Nevertheless, when there is an appreciable ratio (for example,  $> 2$  wt%) of guest molecules doped in host materials, most host molecules are adjacent to a guest molecule.<sup>21</sup> The wave function overlap between neighboring host and guest molecules is substantial and is therefore not the limiting factor for the DET. This analysis therefore reveals that triplet host excitons in this system can lead to guest emission through efficient DET.

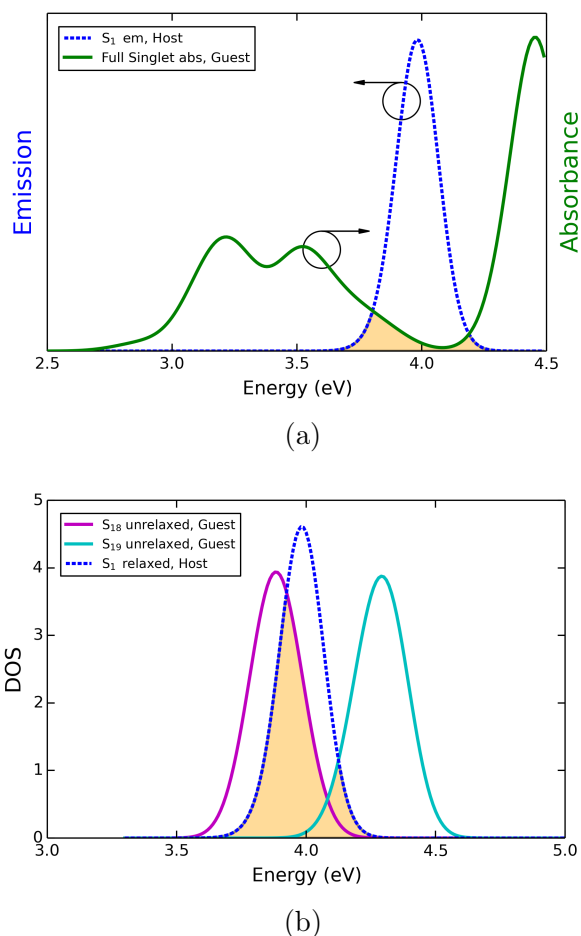


Figure 3: (a) Full singlet absorption spectrum of the guest (in the range of 2.5 to 4.5 eV) compared with  $S_1$  emission spectrum of the host. (b) DOS distributions of unrelaxed  $S_{18}$  and  $S_{19}$  excitons on the guest and relaxed  $S_1$  excitons on the host.

The quenching mechanism for singlet host excitons is more complicated. To better understand the singlet exciton quenching, we also perform a TDDFT/PBE0 calculation on the gas-phase geometry of BTDF and estimate the fluorescence rate of  $S_1$  emission to be  $0.013 \text{ ns}^{-1}$  (Supporting Information). Thus, to efficiently harvest singlet host excitons for guest emission, the energy transfer rate needs to be faster than  $0.013 \text{ ns}^{-1}$ . It can be seen in Figure 2b that there is no DOS overlap between relaxed  $S_1$  excitons of BTDF and unrelaxed  $S_1$  excitons of  $\text{Ir(ppy)}_3$ . It has been shown that efficient energy transfer can take place even in the absence of spectral overlap, which often results from intramolecular through-bond interactions and electronic delocalization.<sup>57–59</sup> However, only intermolecular interactions exist

in our system. Therefore, we expect the energy transfer between such non-overlapping states to be significantly slower than the fluorescence rate of BTDF.

Meanwhile, it is known that the host normally does not emit in PhOLED devices so singlet host excitons must be quenched. Although Ir(ppy)<sub>3</sub> S<sub>1</sub> absorption energy is substantially lower than BTDF S<sub>1</sub> emission energy, it is still possible for singlet host excitons to transfer energy to the guest if Ir(ppy)<sub>3</sub> has absorbing singlet states with energy levels around 4.0 eV. It is therefore interesting to take higher singlet excited states of the guest into consideration. To obtain the full absorption spectrum in the range of 2.5 to 4.5 eV, TDDFT is employed within the QM/MMnonpol framework to compute the first 25 singlet excited states. The full singlet absorption spectrum of guest and S<sub>1</sub> emission spectrum of host are shown in Figure 3a. As can be seen, our results are in good agreement with other TDDFT calculated and experimental spectra for Ir(ppy)<sub>3</sub>.<sup>60</sup> Ir(ppy)<sub>3</sub> has dense singlet energy levels in the shown spectrum range due to the existence of iridium and its symmetric structure, leading to a small overlap between the host S<sub>1</sub> emission spectrum and the guest singlet absorption spectrum. Particularly, Figure 3b indicates that the DOS of unrelaxed S<sub>18</sub> excitons on the guest overlaps considerably with that of relaxed host S<sub>1</sub> excitons.

Within the point-dipole approximation,<sup>61</sup> the FRET rate can be expressed as:<sup>22</sup>

$$k_{FRET} \propto \frac{\kappa^2 J}{R_{DA}^6}, \quad (2)$$

where  $J$  is the spectral overlap and  $\kappa^2$  is the dipole orientation factor. According to Eq. 2, FRET not only relies on the overlap of DOS distributions, but also requires strong absorption and emission intensities. The absorption intensity of Ir(ppy)<sub>3</sub> is weak around 4.0 eV as shown in Figure 3a, where the peak of host S<sub>1</sub> emission spectrum is located on. Nevertheless, we cannot rule out the possibility that efficient resonance energy transfer (RET) can still occur because the point-dipole approximation is restricted to the weak coupling limit.<sup>62,63</sup> When intermolecular distances are similar to molecular dimensions, the Coulomb interaction is

strongly influenced by the shape of the molecular charge distribution. In such strong coupling cases, transition densities need to be considered instead of transition dipoles. It has been shown that even optically dark states can take an active role in RET.<sup>64,65</sup> More complicated methods beyond the simple Förster model are required to treat such problems, including generalized Förster theory and transition density approaches.<sup>66</sup> These methods go beyond the scope of this paper and we show that efficient resonance energy transfer is possible due to the existence of high-lying singlet excited states of Ir(ppy)<sub>3</sub>.

On the other hand, DET is an electron exchange process whose rate only depends on the overlap of DOS distributions. Therefore, effective DET is allowed to occur from singlet host excitons to the high-lying singlet excited states of the guest, as suggested by the significant DOS overlap in Figure 3b. To conclude, in this case, efficient Dexter and resonance energy transfer from singlet host excitons to the guest are both made possible by the high-lying singlet excited states of Ir(ppy)<sub>3</sub>.

## Charge transfer mechanism

In addition to the energy transfer mechanism, the charge transfer mechanism should also be explored, where host excitons break up and then reform on nearby guests. This mechanism is known as the photoinduced electron transfer (PET) process, which plays a key role in a broad range of synthetic and natural systems.<sup>67–69</sup> The Rehm-Weller approach is usually employed to quantitatively predict free energy changes for charge separation and recombination in molecular and supermolecular systems.<sup>70</sup> The free enthalpy change of PET can be computed as:

$$\Delta G_{et} = E^{ox}(D/D^+) - E^{red}(A^-/A) - \frac{e_0^2}{\epsilon r} - \Delta E_{00}, \quad (3)$$

where  $E^{ox}(D/D^+)$  is the donor’s oxidation potential,  $E^{red}(A^-/A)$  is the acceptor’s reduction potential,  $e_0^2/\epsilon r$  is the Coulomb interaction between ions and  $\Delta E_{00}$  is the electronic excitation energy.

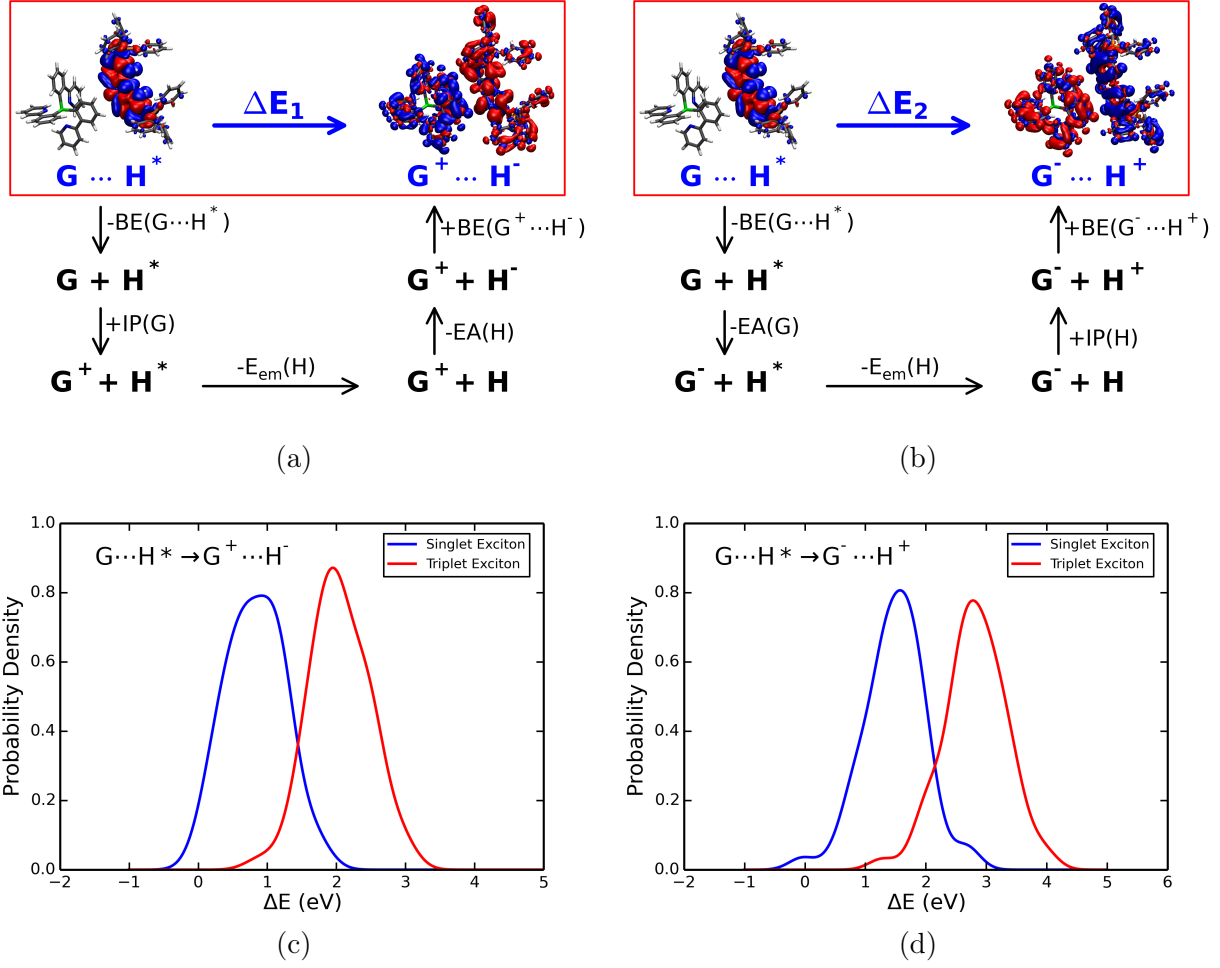


Figure 4: (a) Thermodynamic cycle for computation of the process that a host exciton is dissociated to form a host anion and a guest cation. (b) Thermodynamic cycle for computation of the process that a host exciton is dissociated to form a host cation and a guest anion. (c) The calculated probability distribution of reaction energy for the thermodynamic cycle in (a). (d) The calculated probability distribution of reaction energy for the thermodynamic cycle in (b).

In our host-guest system, the key step is that a local host exciton is dissociated into an electron and a hole on a host-guest (H-G) pair, after which they can recombine on the guest. It is challenging to estimate the reaction energy of this process because the exciton binding energy and the energy difference between singlet and triplet excitons need to be evaluated. Thus, based on the Rehm-Weller approach, we propose to exploit thermodynamic cycles to address this problem and we focus on the exciton dissociation process, as shown in Figure 4. In Figure 4a, the first possible exciton dissociation process is demonstrated: it breaks up to

form a guest cation and a host anion. Here, the binding energy between the guest cation and host anion may be large enough to stabilize the products and reduce the energy barrier considerably. It is therefore natural to investigate the reaction from  $G \cdots H^*$  complex to  $G^+ \cdots H^-$  complex. Five thermodynamic steps are proposed to compute its reaction energy:

1.  $G \cdots H^* \rightarrow G + H^*$ :  $G \cdots H^*$  complex is dissociated into independent G and  $H^*$ .  $BE(G \cdots H^*)$  refers to the binding energy of G and  $H^*$ .
2.  $G + H^* \rightarrow G^+ + H^*$ : a hole is added to the guest.  $IP(G)$  is ionization potential of G.
3.  $G^+ + H^* \rightarrow G^+ + H$ : the host exciton is quenched. Here singlet or triplet emission energy of H is calculated, and marked as  $E_{em}(H)$ .
4.  $G^+ + H \rightarrow G^+ + H^-$ : an electron is added to the host.  $EA(H)$  is electron affinity of H.
5.  $G^+ + H^- \rightarrow G^+ \cdots H^-$ : independent  $G^+$  and  $H^-$  bind together to form  $G^+ \cdots H^-$  complex.  $BE(G^+ \cdots H^-)$  refers to the binding energy of  $G^+$  and  $H^-$ .

As a result, the reaction energy of first exciton dissociation process can be expressed as:

$$\Delta E_1 = -BE(G \cdots H^*) + IP(G) - E_{em}(H) - EA(H) + BE(G^+ \cdots H^-). \quad (4)$$

Similarly, the reaction energy of the other exciton dissociation process (Figure 4b) where a guest anion and a host cation are generated can be calculated as:

$$\Delta E_2 = -BE(G \cdots H^*) - EA(G) - E_{em}(H) + IP(H) + BE(G^- \cdots H^+). \quad (5)$$

To obtain  $EA$ ,  $IP$  and  $E_{em}(H)$ , we perform QM/MMpol calculations on 25 host-guest pairs in 2 snapshots. The distance between centers of mass of each host-guest pair is less than 12 Å to guarantee the electronic coupling for charge transfer is not a limiting factor. Besides, the binding energies need to be calculated for the chosen host-guest pair.

An efficient way to evaluate the binding energy for the host-guest pairs is to employ constrained DFT (CDFT)<sup>71,72</sup> with a polarizable continuum model (PCM).<sup>73</sup> The binding energy  $\text{BE}(\text{G}^+ \cdots \text{H}^-)$  (and  $\text{BE}(\text{G}^- \cdots \text{H}^+)$  similarly) can be calculated as:

$$\text{BE}(\text{G}^+ \cdots \text{H}^-) = \text{E}(\text{G}^+ \cdots \text{H}^-) - \text{E}(\text{G}^+) - \text{E}(\text{H}^-). \quad (6)$$

To obtain  $\text{E}(\text{G}^+ \cdots \text{H}^-)$ , we use CDFT to constrain a positive charge on the guest and a negative charge on the host for a host-guest complex.  $\text{E}(\text{G}^+)$  and  $\text{E}(\text{H}^-)$  are energies of independent guest cations and host anions that can be obtained by normal DFT calculations. As electrostatic interaction is dominant here, we apply the PCM model in all DFT calculations with dielectric constant of the host ( $\epsilon = 2.82$ )<sup>29</sup> to accurately simulate the electrostatic environment.

The binding energy  $\text{BE}(\text{G} \cdots \text{H}^*)$  is more difficult to evaluate. It is hard to constrain the singlet excitation locally on the host molecule of a host-guest complex because the excitation energy of the host is higher than the guest. However, unlike in  $\text{G}^+ \cdots \text{H}^-$ ,  $\text{BE}(\text{G} \cdots \text{H}^*)$  only involves two neutral species, where  $\text{H}^*$  provides a similar electrostatic environment as H. Therefore, we estimate  $\text{BE}(\text{G} \cdots \text{H}^*)$  using the binding energy between ground-state G and H ( $\text{BE}(\text{G} \cdots \text{H})$ ):

$$\text{BE}(\text{G} \cdots \text{H}^*) \approx \text{BE}(\text{G} \cdots \text{H}) = \text{E}(\text{G} \cdots \text{H}) - \text{E}(\text{G}) - \text{E}(\text{H}), \quad (7)$$

where  $\text{E}(\text{G} \cdots \text{H})$ ,  $\text{E}(\text{G})$  and  $\text{E}(\text{H})$  are all computed using normal DFT/PCM.

The results are presented in Figure 4c-4d. As suggested by probability distributions, the reaction energies for both exciton dissociation processes are appreciably uphill by 0.8 eV or more. The triplet host exciton dissociation process has higher energy barrier due to its lower energy. It is also noticed that the energy barrier is lower in the first dissociation process ( $\text{G} \cdots \text{H}^* \rightarrow \text{G}^+ \cdots \text{H}^-$ ) than in the second. However, even for singlet host excitons in first dissociation process, the energy barrier is still substantial, which is due to the large local

exciton binding energy of the host. Therefore, we conclude this charge transfer mechanism for quenching host excitons is unlikely to be efficient. Because exciton binding energies are similar in OLED molecules, this mechanism is probably inefficient for most OLED host-guest systems unless the band offset is massive.

## Conclusions

In conclusion, we have studied the fate of host excitons in a BTDF-Ir(ppy)<sub>3</sub> PhOLED host-guest system using QM/MM simulation. Our results reveal that energy transfer is the primary quenching mechanism for host excitons, while the charge transfer mechanism is unlikely to occur because of high energy barrier for exciton dissociation. Triplet host excitons are harvested through effective Dexter energy transfer to the T<sub>1</sub> state of guest due to excellent spectral overlap. Singlet host excitons, on the other hand, are forbidden from transferring energy to the S<sub>1</sub> state of the guest. Through more detailed analysis, we demonstrate that some of high-lying singlet states of guest overlap substantially with host S<sub>1</sub> state and therefore play a significant role in energy transfer for utilizing singlet host excitons. We note that mechanisms uncovered here may not be general to all OLED host-guest systems. For example, the DET mechanism for quenching triplet host excitons may not be universal as the relaxation of triplet states will largely affect the spectral overlap between the host and the guest. Meanwhile, the singlet exciton energy transfer will depend strongly on the presence and absorption intensity of high-lying excited states of the guest.

Nevertheless, this study provides important insights into better host-guest design. Efficient energy transfer from host to guest can be utilized as an alternative strategy to the energy level alignment. In such case, charge trapping in the guest is not necessary so that better charge carrier mobility and lower driving voltage can be achieved.<sup>20</sup> We also highlight the necessity to evaluate high-lying excited states of the guest in host-guest design because they may be crucial in facilitating energy transfer in host-guest systems. Our future work



should study more different host-guest combinations, take host-guest excimers into account, and investigate the effects of intersystem crossing and non-radiative decay on the exciton quenching mechanisms.

## Acknowledgement

This work was supported by a grant from the U.S. Department of Energy, office of Basic Energy Sciences (Award No. DE-FG02-07ER46474). We thank Dr. Denis Andrienko for providing the force field parameters of BTDF.

## Supporting Information Available

MD and QM/MM simulation details and KDE details for computing probability distributions. Thermodynamic cycle calculation details.

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# Graphical TOC Entry

