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Abstract. Organic light-emitting diodes (OLEDs) show potential as the next-generation solid-state lighting technology. A major barrier to widespread adoption at this point is the efficiency droop that occurs for OLEDs at practical brightness (~ 5000 cd/m²) levels necessary for general lighting. We highlight recent progress in highly efficient OLEDs at high brightness, where improvements are made by managing excitons in these devices through rational device design. General design principles for both white and monochrome OLEDs are discussed based on recent device architectures that have been successfully implemented. We expect that an improved understanding of exciton dynamics in OLEDs in combination with innovative device design will drive future development. © The Authors. Published by SPIE under a Creative Commons Attribution 3.0 Unported License. Distribution or reproduction of this work in whole or in part requires full attribution of the original publication, including its DOI. [DOI: [10.1117/1.JPE.4.040993](https://doi.org/10.1117/1.JPE.4.040993)]

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1 Introduction

Organic light-emitting diode (OLED) is an electroluminescent technology that utilizes stacked layers of organic films several tens of nanometers thick to produce light. OLEDs are currently being used for commercial displays in mobile electronic devices and for televisions. The efficiency, brightness, and lifetime of OLEDs are still the focus of much research aimed at producing better white-light OLEDs so that they can be adopted for solid-state lighting applications.¹⁻⁷ OLEDs are an attractive technology as they are extremely thin and lightweight and can even be fabricated on flexible substrates.⁸

The conversion of electrical to optical power in an OLED occurs through a series of interconnected steps involving injection and transport of charge carriers, formation of tightly bound electron hole pairs known as excitons, and radiative recombination of excitons to yield light. Rather than attempting to understand the details of each step, it is typical in the field to optimize the OLED structure and materials selection with the goal of maximizing the efficiency. This approach has led to the production of commercialized high-efficiency OLEDs, but has left gaps in the understanding of the device physics. In particular, the steps involving excitons are not very well understood. This is understandable considering excitonic devices are still in their infancy compared to electronic and optical devices. As technical specifications for OLEDs become more stringent, emphasis is being placed on understanding the physical processes in an OLED in the hope that one can produce better devices through rational design and materials selection.

In this report, we provide a review on recent advances in the study of OLEDs that originate from an improved understanding of excitons, and we discuss how managing exciton dynamics in an OLED can lead to highly efficient and stable monochrome and white OLEDs.

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2 Background

2.1 Singlet and Triplet Excitons

Excitons are composed of electrons and holes bound by coulomb attraction. As both the electron and hole are fermions with a spin number of $1/2$, the exciton may have a total spin of either 0 or 1. The $S = 0$ and $S = 1$ states are referred to as singlet and triplet excitons, respectively, due to the $(2S + 1)$ degeneracy of each state. Depending on the strength of the coulomb interaction, excitons may be loosely (Wannier-Mott exciton) or tightly (Frenkel exciton) bound. Typically, organic materials have a small dielectric constant resulting in tightly bound Frenkel excitons with the electron and hole quite often localized on a single molecule. For this reason, excitons in organic materials are often referred to as molecular excitations.

2.2 Exciton Formation

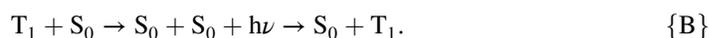
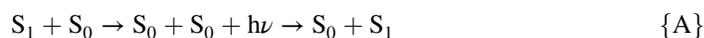
In an OLED, excitons are typically formed at an organic heterojunction by uncorrelated charge carriers (i.e., electrons and holes) injected from opposite electrodes. In the vast majority of practical devices, the ratio of singlet and triplet excitons is 1:3 due to the degeneracy of the two states and assuming similar formation cross-sections, although there have been reports of deviations from this ratio.⁹ Exciton formation will occur primarily at the heterojunction between the electron transporting layer (ETL) and hole transporting layer (HTL) where positive and negative charges tend to accumulate. This region, referred to as the exciton formation zone, is often localized very close to the ETL/HTL interface. This leads to high levels of exciton quenching (see Sec. 2.2) due to coincident high levels of excitons and charges. To broaden the exciton generation zone, materials that have a high minority charge carrier mobility are desirable. If such a material is not available, it is common practice to mix ETL and HTL materials together in a co-host system at the exciton generation zone to create an effective medium that is capable of both electron and hole transport. This medium is often referred to as a co-host.^{6,10}

2.3 Lifetime and Transitions

The lifetimes of singlet excitons ($\sim 10^{-9}$ s) are usually orders of magnitude shorter than those for triplet excitons ($\sim 10^{-3}$ s) since the transition from a triplet excited state to the ground state involves a spin flip which is very slow. For most organic molecules this spin flip occurs over a much longer time scale than the nonradiative triplet to ground-state transition, so most triplet excitons do not contribute to the radiative output of the device. The emission from singlet and triplet states is referred to as fluorescence and phosphorescence, respectively. There are two main strategies to enable triplet emission. The first is to decrease the rate of nonradiative transitions competing with the spin flip. This is usually done by engineering highly deuterated molecules;¹¹ however, this is not a practical approach on an industrial scale. The second is to increase the rate of the spin flip by enhancing spin orbit coupling. Usually these phosphorescent molecules will incorporate a heavy metal atom, such as Ir or Pt.^{12,13}

2.4 Energy Transfer and Diffusion

Excitons may transfer their energy from one molecule (donor) to another molecule (acceptor), forming a new exciton on the acceptor. There are three mechanisms through which an exciton can transfer its energy: light mediated (LM), dipole mediated or Förster, and electron tunneling mediated or Dexter energy transfer. In an LM transfer, the exciton decays radiatively, emitting a photon which is reabsorbed by another molecule.¹⁴



Here, S and T refer to singlet and triplet excitons while the subscripts refer to which excited state the exciton is in (the subscript 0 referring to the ground state). Process B may only occur if

the radiative triplet to ground-state transition and ground to triplet transitions are allowed. This type of transfer occurs over a length scale determined by the absorption length of the acceptor material at the emissive wavelength of the donor molecule.

Förster and Dexter energy transfer both occur without the emission of a photon through one of the following processes:^{15,16}



Förster energy transfer involves the same electronic transitions as LM energy transfer but occurs over much shorter length scales through dipole-dipole coupling of the donor and acceptor molecules rather than through emission of a photon. In this case, the electronic transitions occur within a given molecule, as shown for a singlet excited donor in Fig. 1.

The rate of energy transfer from an excited donor to a collection of acceptors depends on the number and distribution of the acceptors. The energy transfer rate of an immobile donor exciton (a point source) a distance x from a film of acceptors (in a two-dimensional array) is given by the following equation:¹⁷

$$k_{F(\text{thin film})}(x) = \frac{C_A \pi}{\tau} R_0^6 \left[\frac{1}{x^3} - \frac{1}{(x + \Delta)^3} \right], \quad (1)$$

where C_A is the molecular concentration of the acceptors, τ is the lifetime of the donor in the absence of the acceptors, Δ is the thickness of the acceptor film, and R_0 is a characteristic length referred to as the Förster radius, which is defined as the distance at which the rate of energy transfer between an isolated donor-acceptor pair is equal to the energy transfer rate to all other sources. The Förster radius is given by¹⁵

$$R_0^6 = \frac{9 \ln(10) N_A \kappa^2 \Phi_D}{128 \pi^2 n^4} J, \quad (2)$$

where N_A is Avogadro's number, κ is an orientation factor, Φ_D is the donor fluorescent quantum yield, n is the index of refraction of the medium containing the donor and acceptor, and J is the overlap integral of a normalized donor emission spectrum and an acceptor absorption spectrum.

Förster energy transfer for triplet excitons is less common than for singlet excitons and will be discussed further below. Unlike Förster energy transfer, Dexter energy transfer involves the exchange of electrons between the donor and acceptor. In this case, there is a simultaneous exchange of electrons in the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the donor and acceptor, as shown in Fig. 1.

2.5 Bimolecular Exciton Interactions

Excitons may interact with each other and with charge carriers; these interactions often lead to reduced efficiency. Due to their long lifetimes compared to singlet excitons, triplet excitons are more vulnerable to these interactions. Triplet-triplet annihilation (TTA) is considered to be a major source of efficiency roll-off in OLEDs¹⁸ and proceeds as

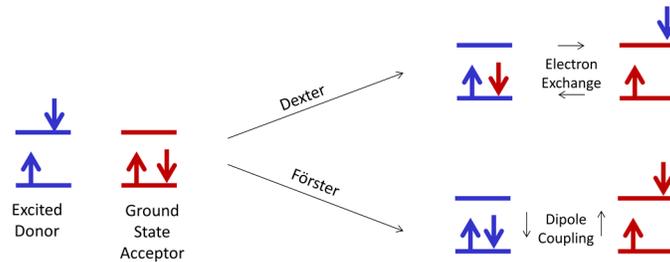
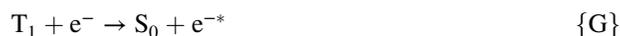


Fig. 1 Electronic transitions involved in Förster and Dexter energy transfer. The upper and lower lines represent the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO), respectively.



When triplets interact, they form an intermediate state, which may lead to an excited singlet or triplet exciton. In most materials, this means processes E and F will occur with a ratio of 3:1, reflecting the formation cross-section of singlet and triplet excitons.

Another major source of efficiency roll-off is triplet polaron annihilation which follows process G or H for electrons and holes.



Here, e^- and h^+ represent electrons and holes in the LUMO and HOMO, respectively, while the asterisk denotes a charge carrier in a higher excited state. Singlet triplet annihilation, singlet polaron annihilation, and singlet-singlet annihilation are also possible loss mechanisms in an OLED that occur to a lesser extent.

While bimolecular interactions reduce the number of excitons that decay radiatively, TTA has been used to increase efficiency in fluorescent OLEDs where triplet excitons do contribute to emission. This is possible through delayed fluorescence, a phenomenon in which the singlet excitons produced through process F are harvested by fluorescent emitters.

The energy levels and mobilities for charge carriers in the various layers of the device as well as the energies of singlet and triplet excitons will be the main parameters influencing how charge carriers and excitons are distributed through an OLED at steady state. Since almost all quenching mechanisms are enhanced when high concentrations of these species are in close proximity, we can use rational device design to try to avoid exciton quenching. Various techniques to reduce the extent of bimolecular interaction will be discussed in the subsequent sections.

2.6 Device Performance

The external quantum efficiency (EQE), η_{ext} , of an OLED can be described by the following equation:

$$\eta_{\text{ext}} = \gamma\chi\Phi_{\text{PL}}\eta_{\text{out}}, \quad (3)$$

where γ is a charge balance factor representing the fraction of charge carriers that pass that from excitons in the device, χ is the fraction of excitons that decay on the emissive dopants, Φ_{PL} is the photoluminescent quantum efficiency of the emissive molecules, and η_{out} is the light outcoupling factor. The focus of much of this report is on increasing χ , or improving the fraction of excitons formed which end up in an emitter molecule.

3 Elimination of Exciton Quenching

3.1 Long-Range Quenching by Nonradiative Centers

Typically, only singlet excitons undergo long-range energy transfer via a Förster mechanism. This is because the transition to ground state from excited triplet states is not formally allowed since spin is not conserved in the transition. In common phosphorescent emitters, however, the triplet to ground-state transition is promoted by enhanced spin orbit coupling induced by the heavy metal atom. Since the radiative triplet to ground-state transition can occur and does so in many cases at a rate much greater than the nonradiative rate, long-range energy transfer via a Förster mechanism becomes possible. Since almost all modern OLEDs rely on phosphors to achieve high efficiency, long-range energy transfer is crucial for many OLED processes. For example, triplet-triplet annihilation and triplet-triplet phosphor energy transfer have both been

shown to follow the distance dependences predicted by Förster's theory.^{18–20} It was also pointed out by Förster himself in his initial formulation that his mechanism would be applicable to triplets if the radiative triplet to ground-state transition could compete with the nonradiative transition¹⁵ and was first experimentally verified not long afterward.²¹

We have shown that since phosphorescent emitters can interact through a Förster mechanism, exciton quenching centers can have a large influence on device performance even when they are not inside the emissive zone. We placed a layer of C_{60} molecules close to the emissive zone and measured the fraction of excitons captured by this layer.²² Any excitons captured by C_{60} rapidly decay nonradiatively, thus simulating other nonradiative quenching centers that can occur in regular devices. The results, shown in Fig. 2, indicate that even quenching centers far outside the emissive zone can contribute significantly to exciton quenching. The results match well with predictions based on exciton transfer from the phosphorescent emitters to C_{60} via a Förster-type mechanism using a simple model based on Eq. (1).

3.2 Elimination of Accumulated Charges at Organic Heterojunctions

3.2.1 Simple device structure

Traditionally, high-efficiency OLEDs have incorporated many different organic layers, each meant to serve a specific function such as charge injection, charge transport, efficient energy transfer to emissive dopants, or minority carrier blocking. We have shown that contrary to conventional wisdom in the field, many layers are not necessary to achieve high-efficiency devices, but rather reduce the device efficiency through exciton quenching and loss of charge balance due to charge carriers built up at interfaces. Exciton quenching in phosphorescent OLEDs is particularly difficult to control since excitons have the potential for long-range interaction with nonradiative quenching centers, as demonstrated in Sec. 3.1. Several different device

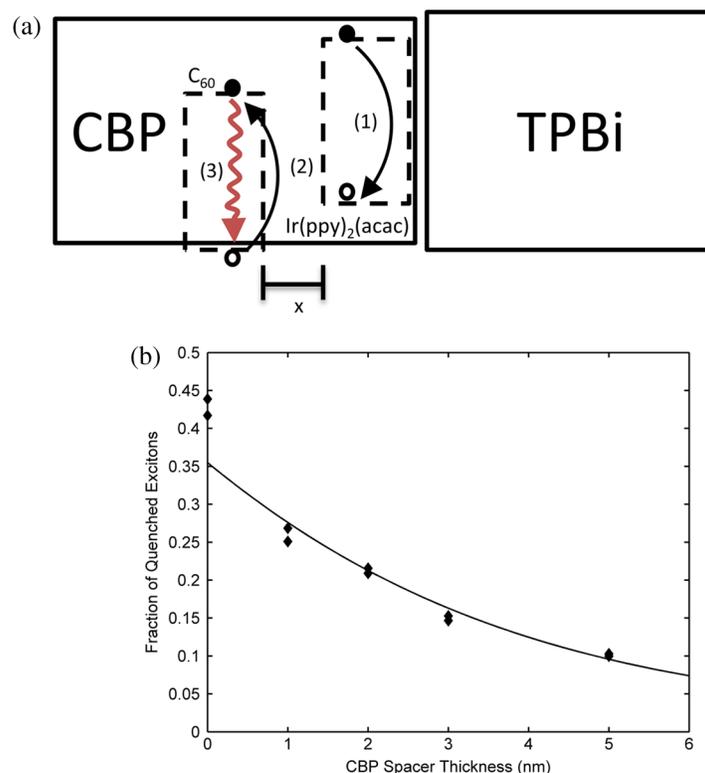


Fig. 2 (a) Decay of bis(2-phenylpyridine)(acetylacetonate)iridium(III) [$Ir(ppy)_2(acac)$] (1) and simultaneous excitation of C_{60} (2) followed by subsequent rapid nonradiative decay of C_{60} . (b) Fraction of excitons quenched by a layer of C_{60} molecules as a function of the separation between the emissive layer and the C_{60} layer (diamonds) and prediction based on a simple model of quenching via Förster-type energy transfer (solid line).²²

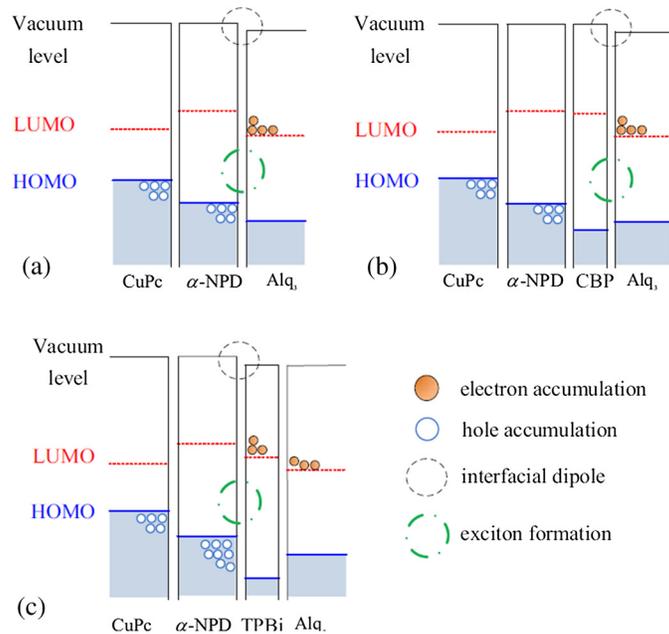


Fig. 3 Schematic energy-level diagram for three devices, depicting charge carrier accumulation, interfacial dipoles, and exciton formation. (a) shows the standard structure, while in (b) inserting a thin CBP spacer next to the exciton generation zone reduces the amount of accumulated charge at the exciton generation zone, improving the device performance. In (c) using a TPBi spacer, instead, does not separate exciton generation and charge accumulation.²³

configurations are depicted in Fig. 3, where the device in Fig. 3(b) has the highest efficiency since the exciton generation zone is separated from regions of major charge accumulation. Also, note that the amount of accumulated charge is dependent on the energy level offset at the heterojunction. We can reduce the amount of built-up charge at interfaces further by adopting a simplified device structure with closely matched energy levels depicted in Fig. 4.

Using the simplified device structure incorporating only three organic materials shown in Fig. 4, we have demonstrated an OLED with an EQE of 24.5% at a brightness of 1000 cd/m². This device contains only a single organic heterojunction between 4'-bis(carbazol-9-yl)biphenyl (CBP) and 2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi), with closely matched HOMO and LUMO levels to reduce charge accumulation.

3.2.2 Co-host device structure

This section will discuss the advantages of using a co-host for high-efficiency OLEDs, and, in particular, the focus is on recent high-efficiency devices fabricated using co-hosts. In a co-host structure, the emissive layer (EML) is a mixture of an ETL and HTL material rather than a single material. The use of co-hosts provides an engineering solution to problems in synthesizing materials that exhibit high mobilities for both hole and electron transport. Rather than waiting for

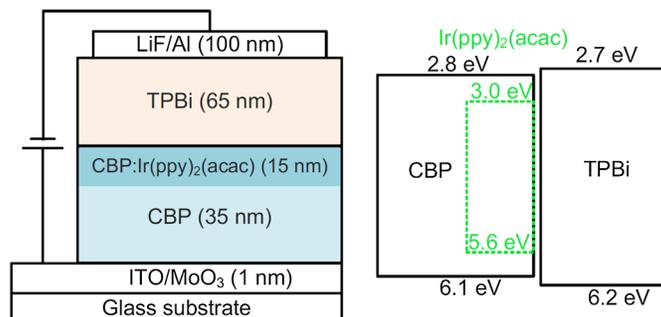


Fig. 4 Highly simplified OLED design.²⁴

new ambipolar materials (which are desirable as host materials) to be developed, engineers can use existing materials through the co-host method to create an effective medium capable of transporting electrons and holes.

In addition to the ambipolar character of co-hosts, they also improve device efficiency by removing the charge transport barriers to the EML that are present in traditional OLEDs, as can be seen in the co-host structure shown in Fig. 5. We have previously demonstrated that the build-up of charges and loss of charge balance due to energetic barriers to charge transport can contribute significantly to efficiency roll-off.²⁴

The co-host design can also reduce charge trapping on the emissive dopants for carefully chosen combinations of materials. For a typical single-host OLED device, the bandgap of the host must be significantly larger than that of the emitter in order to confine excitons onto the dopants. This leads to large differences in the HOMO and/or LUMO levels of the host and dopant, which lead to charge trapping on the dopants. This build-up of trapped charge can contribute to exciton-polaron quenching and efficiency reduction. By matching the HOMO level of the HTL and the LUMO level of the ETL to the HOMO and LUMO of the dopant, as shown in the structure in Fig. 5, this charge trapping can be minimized in a co-host structure. Using a co-host in the EML has also been demonstrated to broaden the exciton formation zone, leading to a decreased efficiency roll-off since high concentrations of excitons associated with a narrow exciton generation zone are avoided.

Using the device structure shown in Fig. 5, an OLED with peak EQE and power efficiencies of 29.1% and 124 lm/W was achieved. In addition to these impressive numbers, the device also demonstrated a very low roll-off due to a reduced exciton-polaron quenching. It is also worth noting that the turn-on voltage of 2.4 V is as low as the triplet energy of the emitting dopant.

On top of the advantages derived from the use of a co-host structure, another boost to efficiency originates in the dipole orientation of the emitters. Angle resolved photoluminescence (PL) was used to determine that 77% of the dipoles were oriented horizontally compared to an expected 67% for isotropically oriented dipoles.²⁵ Based on these results, a predicted outcoupling efficiency of 28.3% is taken with a peak EQE of >29%; this suggests a near-unity internal quantum efficiency. An in-depth analysis of the optics of this device, including an experimental outline for predicting the maximum achievable EQE using simple methods, has been carried out by the same group.²⁵

Using the same co-host framework, OLEDs with multiple dopants have also been demonstrated.²⁶ An orange OLED was fabricated using the device architecture shown in Fig. 6. These researchers were able to achieve a very high EQE of 25.0% with a low roll-off.

We should point out that despite the performance demonstrated by the co-host structure described above, the added complexity of using a co-host over a standard, single-host EML may be a major deterrent for a broader adoption of this or similar types of devices.

4 Exciton Harvesting

4.1 Exciton Harvesting Working Principle

In most OLEDs, excitons will be formed primarily on the host material at the interface between the HTL and ETL. These excitons will then diffuse away from the interface and, in efficient

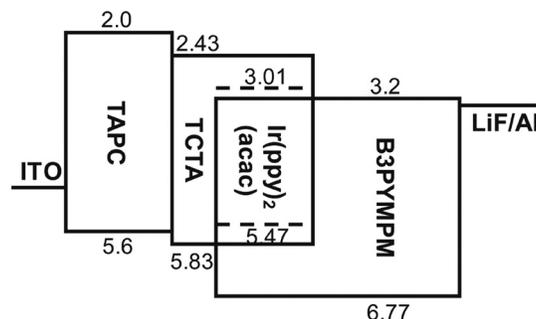


Fig. 5 Device structure and energy levels of the exciplex forming co-host structure.¹⁰

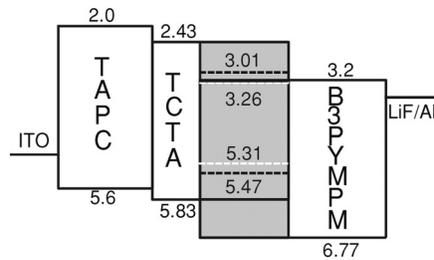


Fig. 6 Device structure and energy-level diagram of the orange OLED using a co-host.²⁶

devices, transfer their energy to an emissive dopant through either Förster or Dexter energy transfer. The energy transfer efficiency between host and dopant is dependent on the molecules used. When a new color of OLED is desired, it is often necessary to change the host and/or transport materials in order to find a combination of materials that will produce a high-efficiency OLED. To avoid this, we can instead separate the functions of exciton harvesting and emission by incorporating one dopant that has high energy transfer efficiency when paired with the desired host and another with the desired emission wavelength. Once excitons are harvested by the first dopant, the energy can be efficiently passed on to the second dopant through a well-understood Förster process. Typically, an emissive dopant with a lower triplet energy than the harvesting dopant is necessary so that the exciton transfer is exothermic. The concept of exciton harvesting may be used in two different device configurations: co-doping of an exciton harvesting and emitting dopant either into the same region of a host or into adjacent layers in the OLED. The two strategies are referred to as intrazone and interzone exciton harvesting, respectively.

This strategy of separating desired functions onto different molecules follows a pattern of success in OLED development. Early improvements in efficiency of OLEDs were achieved by separating the functions of electron and hole transport by using an HTL and an ETL rather than a single organic layer.²⁷ Later, the functions of charge transport and emission were separated by using an emissive dopant in addition to the transport layers.²⁸ This exciton harvesting strategy represents another natural step in the separation of different functions by using separate exciton harvesting and emissive molecules.

We can understand the improvement in performance as related to Eq. (3) by extending the equation to include the exciton harvesting ability of the exciton harvesting dopant (donor) and emissive dopant (acceptor).²

$$\eta_{\text{ext}} = \gamma\eta_{\text{out}}\{\chi_A\phi_{\text{PL},A} + \chi_D[\eta_{D-A}\phi_{\text{PL},A} + (1 - \eta_{D-A})\phi_{\text{PL},D}]\}, \quad (4)$$

where χ_D and χ_A denote the fractions of excitons that are trapped in the donor and acceptor molecules, respectively, Φ_{PL} is the quantum yield of the emitters, and η_{D-A} stands for the energy transfer efficiency from donor to acceptor, i.e., from green to yellow or red phosphorescent emitters. The exciton harvesting strategy functions by maximizing χ_D and η_{D-A} by choosing a donor that efficiently harvests excitons and an acceptor with a high donor acceptor energy transfer efficiency. This process is further depicted in Fig. 7.

Energy transfer efficiency between dopants can be measured using transient PL measurements such as those depicted in Figs. 8(a) and 8(b). The lifetime of green dopants in a host film are measured as a function of total concentration of the donor and acceptor dopants. As the dopant concentration increases, the energy transfer efficiency from donor to acceptor increases, as shown in Fig. 8(c), with the energy transfer efficiency reaching >90% at high dopant concentrations.

4.2 Intrazone Triplet Exciton Harvesting

Rather than searching for new host-dopant combinations that provide high efficiency when a new emitter color is needed, we can instead take advantage of the proven performance of the CBP/Ir(ppy)₂(acac) host/emitter combination, where Ir(ppy)₂(acac) is bis(2-phenylpyridine)(acetylacetonate)iridium(III). OLEDs using CBP and Ir(ppy)₂(acac) as host and dopant

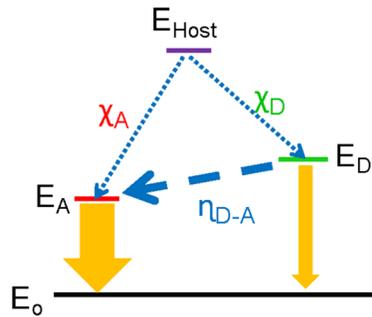


Fig. 7 Schematic diagram of energy transfer processes in a two-dopants system. The dopants may be doped in the same region or in adjacent regions of a single host. E_{HOST} , E_A , E_D , and E_0 represent the energy levels of the host, acceptor molecule, donor molecule, and the ground state, respectively. χ_A , χ_D , and η_{D-A} are as defined in Eq. (4).

have been shown to have high efficiency,²⁴ suggesting that $\text{Ir}(\text{ppy})_2(\text{acac})$ is an especially good exciton harvester in this material system. It is not entirely clear whether the exciton harvesting ability of $\text{Ir}(\text{ppy})_2(\text{acac})$ arises from its high rate of host dopant energy transfer, or its hole trapping ability and subsequent dopant exciton formation, or both. However, there are some indications that hole trapping may play a role.³⁰ Attempts at replacing $\text{Ir}(\text{ppy})_2(\text{acac})$ with a red dopant molecule bis(2-methyl-dibenzo[f,h]quinoxaline)(acetylacetonate) iridium (III) [$\text{Ir}(\text{MDQ})_2(\text{acac})$] leads to an EQE of 17.3% in an optimized device.

Rather than searching for a new set of transport and host materials compatible with $\text{Ir}(\text{MDQ})_2(\text{acac})$ or searching for a red emitter with better exciton harvesting ability in CBP, one instead may use the intrazone exciton harvesting method. The device structure shown in Fig. 9(a) includes an EML consisting of CBP co-doped with both $\text{Ir}(\text{ppy})_2(\text{acac})$ (2 wt%) and $\text{Ir}(\text{MDQ})_2(\text{acac})$ (2 wt%). The exciton harvesting strategy was successfully used in this case to improve the efficiency of the red OLED.³⁰ Co-doping $\text{Ir}(\text{ppy})_2(\text{acac})$ (2 wt%) with $\text{Ir}(\text{MDQ})_2(\text{acac})$ (2 wt%) in CBP leads to emission almost entirely from $\text{Ir}(\text{MDQ})_2(\text{acac})$ dopant with a max EQE of 24.8%, as shown in Fig. 9(b).

In this intrazone exciton harvesting scheme, both Dexter- and Förster-type energy transfers are possible between the exciton harvester and emitter. Dexter energy transfer is likely to play a smaller role since it is a short-range mechanism limited to nearest neighbors and the low concentrations of both the harvester and emitter mean that only a small number of exciton harvesting dopants will have an adjacent emitter.

4.3 Interzone Exciton Harvesting

We have also demonstrated the interzone exciton harvesting method using adjacent layers of CBP: $\text{Ir}(\text{ppy})_2(\text{acac})$ (8 wt%) and CBP: $\text{Ir}(\text{MDQ})_2(\text{Bpz})$ (8 wt%), where $\text{Ir}(\text{MDQ})_2(\text{Bpz})$ is [bis(2-methyl-dibenzo [f,h]quinoxaline) tetrakis(1-pyrazolyl)-borateiridium(III)].¹ Without the exciton harvesting method, the optimized device using $\text{Ir}(\text{MDQ})_2(\text{Bpz})$ as a dopant in CBP was able to achieve an EQE of 15.2% at 1000 cd/m². By using the interzone exciton transfer method, the EQE was increased to 21.5% at the same luminance level. The structure with a harvesting layer is shown in Fig. 10(a). EQE and power efficiency for the devices with and without the aid of interzone exciton harvesting are shown in Fig. 10(b).

In this interzone exciton harvesting scheme, energy transfer will be dominantly the Förster type, although it is still possible to have Dexter energy transfer at the interface between the exciton harvesting and emitting layers. Förster energy transfer does not require the exciton harvesting and emitting molecules to be adjacent to each other, and, in practice, Förster energy transfer between dopants is usually efficient for separations $< \sim 3$ nm.¹ When choosing a thickness for the exciton harvesting layer, we are limited to the range over which the exciton harvesting dopants can efficiently pass their energy to the emitters, which explains the choice of a 3-nm-thick exciton harvesting layer in the device shown in Fig. 10(a). In situations where an ~ 3 -nm-thick exciton harvesting layer is not sufficient to capture the excitons passing through

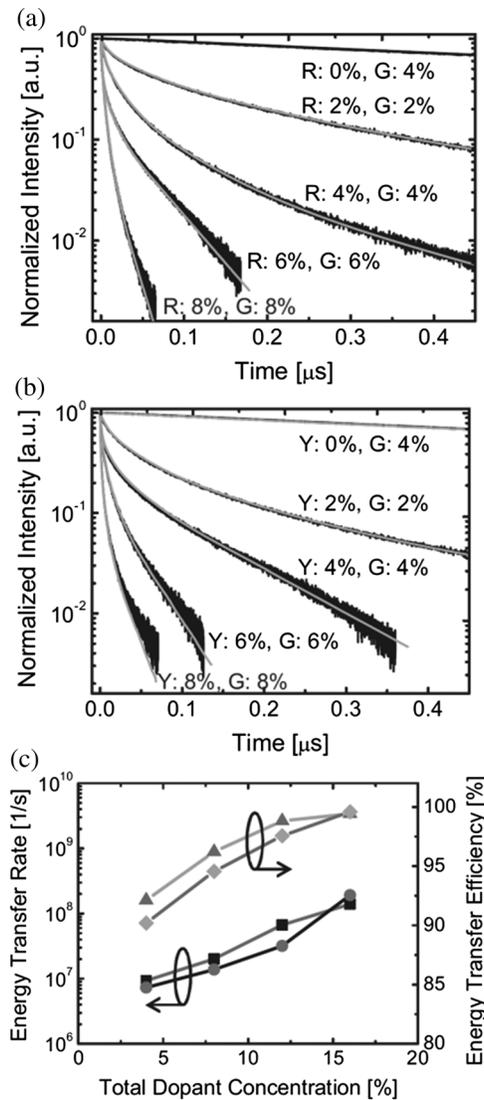


Fig. 8 Solid-state transient response of (a) red and green co-doped CBP films and (b) yellow and green co-doped CBP films at various co-doping concentrations. The solid lines are the exponential fits to the transient decay responses. The excitation wavelength is at 350 nm. (c) Calculated energy transfer rate and efficiency versus total dopant concentration with the control sample concentration corresponding to the green donor concentration of the co-doped films. Triangles (squares) and rhombuses (circles) denote the energy transfer efficiency (energy transfer rate) of co-doped yellow and red emissive films, respectively.²⁹

the emitter layer, the intrazone exciton harvesting scheme is preferable. It is also worth noting that the concentrations of both harvesting and emissive dopants are typically higher in the interzone exciton harvesting relative to intrazone exciton harvesting scheme. The higher dopant concentrations are necessary to maintain efficient harvester-emitter energy transfer.

5 Design Principles for White OLEDs

5.1 Exciton Harvesting for White OLEDs

Given the success of exciton harvesting with different emissive dopants, this technique is a natural fit for engineering white OLEDs that require highly efficient emission at multiple wavelengths. In this situation, we again benefit from the exciton harvesting method as it allows us to select dopants with the desired wavelengths rather than compromising to achieve good host/dopant energy transfer (as long as

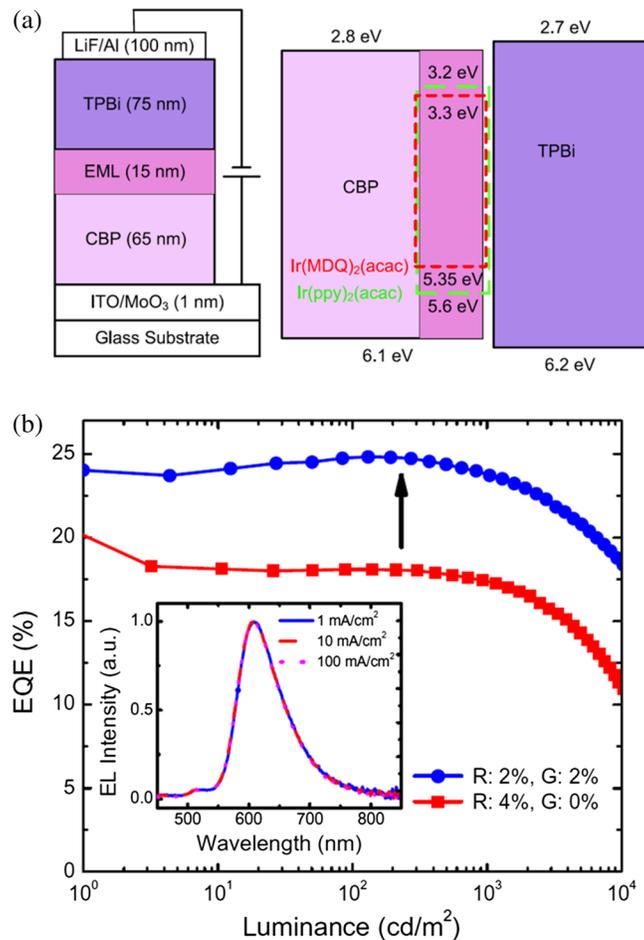


Fig. 9 (a) Schematic device structure and corresponding energy-level diagram of the device and (b) external quantum efficiency (EQE) versus luminance comparison between the optimized co-doped device and optimized solely red-doped device. Inset shows the electroluminescence (EL) spectra of the optimized co-doped device under a wide range of current densities.³⁰

the energy transfer from the harvesting to emitting dopant is exothermic). We demonstrated a highly efficient white OLED using multiple intrazone exciton harvesting layers with a 24.5% EQE at 1000 cd/m^2 with a color rendering index (CRI) of 81, and an EQE at 5000 cd/m^2 of 20.4% with a CRI of 85, using standard phosphorescent emitters.²⁹ The optimized device used iridium (III) bis(4,6-difluorophenyl-pyridinato-N,C2')(picolinate) as the blue emitter, $\text{Ir}(\text{ppy})_2(\text{acac})$ as the green emitter, and intrazone exciton harvesting layers using $\text{Ir}(\text{ppy})_2(\text{acac})$ as the exciton harvester co-doped with $\text{Ir}(\text{BT})_2(\text{acac})$ and $\text{Ir}(\text{MDQ})_2(\text{acac})$ as the yellow and red emitters, respectively, as shown in Fig. 11(a). Note that while there may be some exciton transfer between the different emitting layers, the excellent device performance is mainly due to the intrazone exciton harvesting within both the red and yellow emitting layers.

5.2 Fluorescent/Phosphorescent Hybrid OLEDs

The use of phosphorescent emitters in OLEDs allows us to harvest triplet excitons that would otherwise not contribute to the radiative output of the device, allowing us to achieve $\sim 100\%$ internal quantum efficiency. Blue phosphorescent emitters, however, tend to be unstable compared to green and red emitters, leading to device degradation over time as the energy necessary to excite the molecules is close to the energies of the C-C and C-N bonds in the molecule. In white OLEDs, one solution to the instability of blue phosphorescent emitters is to use a blue fluorophore in combination with lower-energy phosphorescent emitters as the emitters instead of an all-phosphorescent device. In principle, these hybrid OLEDs still potentially allow us to

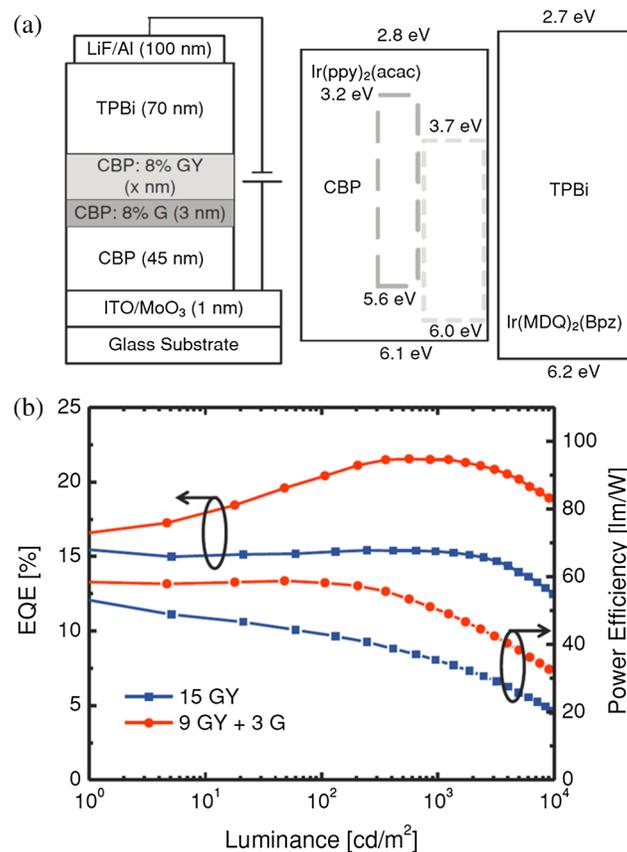


Fig. 10 (a) Device configuration of an OLED using the interzone exciton harvesting strategy. (b) EQE and power efficiency of an OLED with a 15-nm-thick emissive layer (EML) of only the green-yellow dopant compared to an EML with 9 nm of the green-yellow dopant and 3 nm of the green dopant.¹

achieve 100% internal quantum efficiency if the blue fluorophore can harvest all of the singlet excitons. This strategy can help maintain color balance in a white OLED since the 1:3 ratio of singlet to triplet excitons typically formed under electrical excitation in organic materials coincidentally matches up fairly well with the requirement that $\sim 25\%$ of the white light be in the blue region. The difficulty with this strategy is ensuring that singlet and triplet excitons are captured and decay on the appropriate molecules. Any triplet excitons captured by the blue fluorophore will be lost as the radiative triplet to ground-state transition is not allowed in fluorescent molecules. This leads to the requirement that triplet energy transfer from other sources to the fluorescent molecule is energetically unfavorable. In addition, any singlet excitons captured by the lower-energy phosphorescent emitters reduces the blue emission to insufficient levels. In order to achieve a high-efficiency device and maintain high-quality white light, OLEDs must be carefully designed to control exciton capture and the transfer of excitons between the various emitters.

5.2.1 Single emitting layer

The simplest way to incorporate a blue fluorophore into the device is to use a fluorescent host material that also has the desired emissive properties. This allows a simple one-EML architecture to be used; however, this one-EML design has several potential drawbacks. One such drawback relates to the difficulty in finding a set of host/dopant molecules that have the desired properties; a host must be an ambipolar charge transporter and have efficient energy transfer to dopants, and the emitter(s) must have high fluorescent quantum yield. It is also difficult to control energy transfer between the different emitters in a single-layer structure. Energy transfer from the blue to lower-energy emitters is unavoidable in a single-layer configuration, which usually

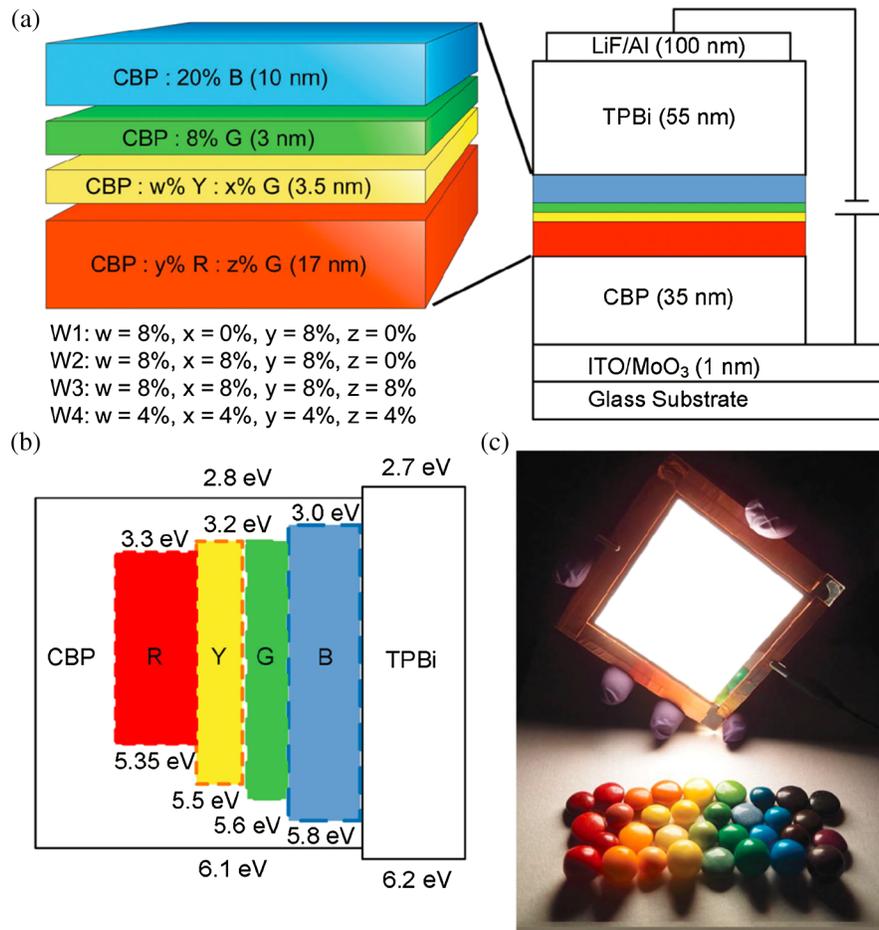


Fig. 11 Device configurations (a) and energy-level diagrams (b) for white OLEDs (WOLEDs) W1 to W4. The dopants employed are Flrpic for blue (B), Ir(ppy)₂(acac) for green (G), Ir(BT)₂(acac) for yellow (Y), and Ir(MDQ)₂(acac) for red (R). All doping concentrations are in wt%. (c) A photo of a large area (80 mm \times 80 mm) WOLED (W3) illuminating at 5000 cd/m² with a color rendering index of 85.²⁹

leads to insufficient blue emission and downconversion losses. Energy transfer from the phosphorescent emitter back to the fluorophore is also possible if the triplet energy of the fluorophore is close to or lower than that of the phosphorescent emitters. This can be mitigated by choosing a blue emitter that has a small singlet-triplet splitting. Most molecules with this property also tend to have a reduced fluorescent quantum efficiency, although there has been progress in engineering molecules with the desired properties.³¹ Despite these challenges, high-efficiency, single-layer hybrid white OLEDs have been fabricated. For example, Ye et al. synthesized a sky blue fluorophore 2,8-di[4-(diphenylamino)phenyl] dibenzothiophene-S,S-dioxide and demonstrated that a single-layer hybrid white OLED using a common orange phosphorescent emitter could be fabricated with a maximum total EQE, current efficiency (CE), and power efficiency (PE) of 26.6%, 53.5 cd A⁻¹, and 67.2 lm W⁻¹, respectively. The spectra and EQE and power efficiency can be seen in Figs. 12(a) and 12(b), respectively.

Although the efficiency of this device is impressive, the electroluminescence spectra in Fig. 12(a) shows a poor color stability. In addition, the use of only two emitters and suboptimal blue emission in this device and other single-EML hybrid white OLEDs leads to poor color rendering index.

Liu et al. synthesized a blue emitting host 4-(4,6-diphenoxy-1,3,5-triazin-2-yl)-N,N-diphenylaniline (POTA) and managed to fabricate a device with a power efficiency of 59.8 ± 1.0 lm W⁻¹ and a maximum external quantum efficiency of $24.7 \pm 0.7\%$ using green and red phosphorescent emitters in addition to the blue emitting host.³ The emission spectra and

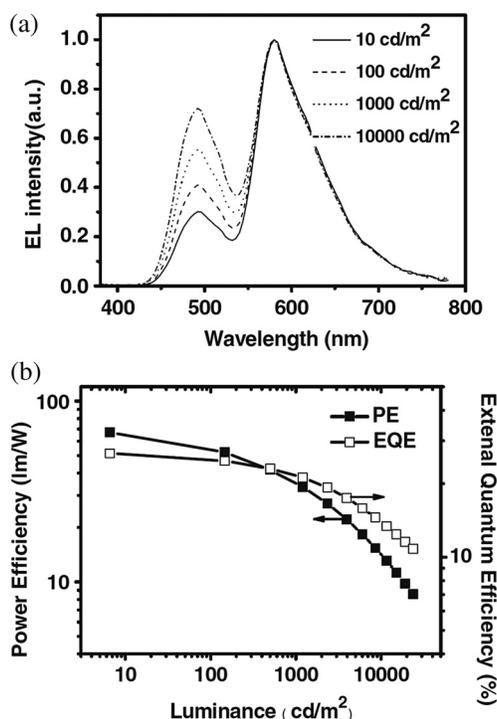


Fig. 12 (a) EL spectra at different brightness and (b) power efficiency and EQE as a function of brightness of the single-layer, two-emitter hybrid white OLED.³¹

the EQE and power efficiency can be seen in Figs. 13(a) and 13(b), respectively. The high performance of this device is due to the small singlet-triplet splitting and a high fluorescence efficiency of POTA; both parameters were simultaneously achieved using a structure with a donor and acceptor subunit connected by a pi-conjugated bridge. Unfortunately, this device also showed poor color stability, but managed to achieve an impressive EQE with a better white output than a two-emitter device.

5.2.2 Multiple emissive layers

In order to achieve better control over the interplay among emitters, a multiple-emissive zone structure is used where the blue fluorescent-emissive zone is spatially separated from the phosphorescent-emissive zone or zones. In this case, a fluorescent blue dopant will usually be doped into a wider-bandgap host. This removes some of the constraints, such as ambipolar transport ability and efficient host-dopant energy transfer that were placed on the fluorophore in single-EML devices. In contrast to the single-layer method, which depends strongly on new materials to advance the device performance, multiple EML provides opportunities in innovative device architectures to improve performance in hybrid white OLEDs.⁴⁻⁶ In order to avoid energy transfer between fluorophores and phosphors, a thin spacer layer of undoped host material is often used between the blue and lower-energy emissive regions. The spacer is typically 2- to 3-nm thick, a length over which a significant Förster energy transfer from the blue to lower-energy dopants can occur for most dopants. Transfer of triplet excitons from the phosphorescent emitters to the fluorophore may also occur if no spacer layer is used and the transfer is energetically favorable. The use of spacer layers is undesirable since an undoped spacer in the EML reduces the power efficiency as well as the EQE due to increased driving voltage and nonradiative losses on the host, respectively. Spacer layers and spatially separated emissive layers also tend to cause a large color drift as the exciton generation zone shifts at various driving voltages. The use of co-hosts has been used to mitigate both of these issues.

A spacer layer composed of a mix of an electron transporting material and hole transporting material shows superior performance and color stability compared to the one composed of only a single material.^{4,5} By tuning the relative concentrations of the electron and hole transporting

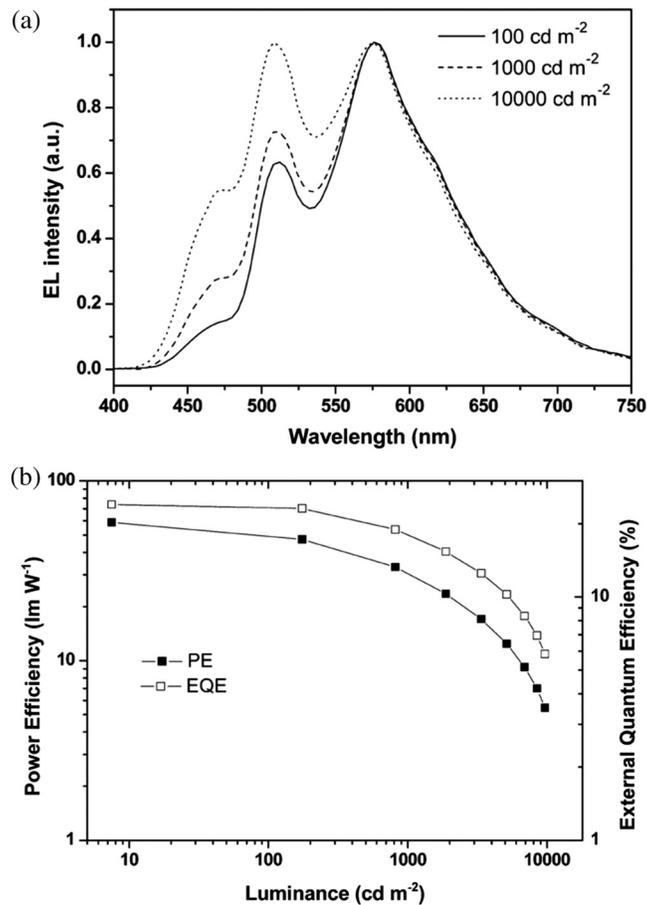


Fig. 13 (a) Electroluminescent spectra at a variety of luminance levels showing a color drift and (b) EQE and power efficiency of the three-emitter single-layer hybrid white OLED.³

components, the carrier concentrations in the device could be influenced, allowing for a decrease in accumulated space charge which quenches excitons. The use of a mixed spacer layer also spreads out the exciton generation zone, which also helps to boost performance. Using this technique, Zhao et al. have demonstrated hybrid white OLEDs with EQE's of $\sim 14\%$ at 1000 cd/m^2 .^{4,5}

Extending this concept, it was demonstrated that doping the fluorophore into a co-host allowed the removal of the spacer layer entirely, leading to a dramatic increase in performance.⁶ The device, whose structure and performance are shown in Figs. 14(a) and 14(b), has an EQE of 17% at 1000 cd/m^2 and a peak EQE of 19%. In this device, a low concentration of the blue fluorescent dopant was used to limit the Dexter energy transfer from phosphorescent green dopants in the adjacent layer to the nonemissive triplet state of the blue fluorophore, which represents a loss mechanism in the device. In addition, the use of a co-host broadened the exciton formation zone and shifted it away from the interface between the blue and green doped regions. This decreased the extent of energy transfer from the blue fluorophore to the lower-energy dopants, which leads to insufficient blue emission in many hybrid white OLEDs. In addition, by eliminating the need for a spacer layer, there were no losses due to exciton diffusion through an undoped spacer. The various energy transfer pathways for singlet and triplet excitons in the device are depicted in Fig. 14(a).

6 Conclusion

The paper presented an overview of various techniques available to manage excitons leading to extremely high efficiencies. Removing energy barriers at heterojunctions in the device, either

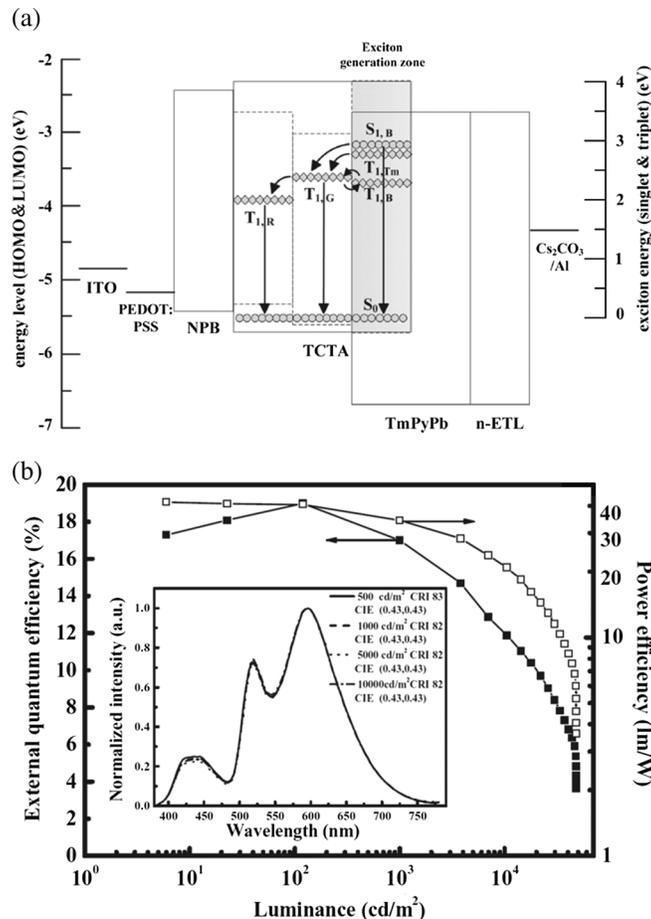


Fig. 14 (a) Energy-level scheme for materials used in the hybrid WOLED, and exciton (S_0 , S_1 , and T_1) energy diagram of the emitter layers. The gray-filled rectangle represents the main exciton generation zone. R, G, B, and Tm represents Ir(MDQ)₂(acac), Ir(ppy)₂(acac), 4P-NPD, and TmPyPb, respectively. Solid lines and dashed lines correspond to HOMO and LUMO energy levels, respectively; circles and diamonds refer to the exciton (S_0 , S_1 , and T_1) energies, respectively. (b) External quantum efficiency and power efficiency versus luminance characteristics of the optimized device. The inset shows the normalized EL spectra at different brightness levels.⁶

through a simplified device structure or use of a co-host design, was shown to reduce exciton quenching and lead to high-efficiency devices. The importance of Förster-type interactions in these quenching processes was also emphasized. Managing exciton formation and a control of energy transfer between emissive dopants are shown to be useful tools for improving efficiency. Techniques for optimal exciton harvesting using interzone and intrazone device designs are shown to be widely applicable to a variety of OLEDs. The challenges involved in using a fluorescent blue dopant were also discussed, and tools to manage both triplet and singlet excitons are described. The latest improved understanding of exciton dynamics in OLEDs in combination with innovative device design will certainly help guide future research and the development of OLEDs for applications ranging from flat-panel displays to solid-state lighting.

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