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ORGANIC LIGHT-EMITTING TRANSISTORS

Towards the Next Generation
Display Technology

MICHELE MUCCINI
STEFANO TOFFANIN

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1

INTRODUCTION

This book is focused on organic light-emitting transistors and on their characteristics, which make them a potentially disruptive technology in a variety of application fields, including display and sensing. The distinguishing feature of this class of devices is the use of a planar field-effect architecture to combine in a single-structure electrical switching, electroluminescence generation, and photon management in organic materials.

Organic semiconductors are carbon-rich compounds with a structure tailored to optimize functions, such as charge mobility or luminescent properties. A distinguishing factor resides in the multiple functionalities that organic materials can sustain contemporarily when properly tailored in their chemical structure. This may allow the fabrication of multifunctional organic devices using extremely simple device structures and, in principle, a single active material. Indeed, in a molecular solid in which the constituting units are molecules held together by weak van der Waals forces, the optical properties are dominated by excitons, which are molecular excited states that are mobile within the solid. Excitons can hop from molecule to molecule or, in the case of polymers, from chain to chain as well as along the polymer backbone, until it recombines generating light in a radiative process. Similarly, charge carrier (electron or hole) transport can occur via hopping between molecular sites or from chain to chain. In this case, the carrier mobilities are quite low compared with inorganic semiconductors, whose room temperature values

typically range from 100 to 10^4 cm²/Vs. In contrast, in highly ordered molecular materials where charges hop between closely spaced molecules forming a crystalline stack, mobilities of less than 1 cm²/Vs have been observed at room temperature. This is an approximate upper bound, with the mobility ultimately limited by thermal motion between neighboring molecules. Low mobility leads to low electrical conductivity and also results in a very low charge carrier velocity, which one has to consider as an intrinsic factor when evaluating the practical applications of organic semiconducting materials.

The weak van der Waals forces typical of molecular solids decrease as $1/R^6$, where R is the intermolecular spacing. This is in contrast to inorganic semiconductors that are covalently bonded, whose strength falls off as $1/R^2$. Hence, organic electronic materials are soft and flexible, whereas inorganic semiconductors are hard, brittle, and relatively robust when exposed to adverse environmental agents, such as moisture, corrosive reagents, and plasmas, commonly used in device fabrication. The apparent fragility of organic materials has also opened the door to a suite of innovative fabrication methods that are simpler to implement on a large scale than has been thought possible in the world of inorganic semiconductors.

The most appealing property of organic materials for electronic and photonic applications is that they can be deposited on virtually any substrates, including silicon backplanes and low-cost ones such as plastic, metal foils, and glass. Organic materials are compatible with low-cost fabrication methods that can be implemented on a large scale, such as vacuum sublimations and solution-based processes. This fundamental advantage and the low amount of material used in thin-film devices position them favorably to fill the application markets where cost is a key factor and the requirements on performances do not impose the use of high-performing inorganic semiconductors.

Organic electronics are beginning to make significant inroads into the commercial world, and if the field continues to progress at its current pace, electronics based on organic thin-film materials will soon become a mainstream of our technological existence. Already products based on active thin-film organic devices are in the marketplace, most notably the displays of several mobile electronic appliances. Yet, to unravel the greater promise of this technology with an entirely new generation of ultralow-cost, lightweight, and even flexible electronic devices, new and alternative solutions must be identified to overcome the limitations currently faced with the existing device architectures.

Indeed, the vertical-type structure of organic light-emitting diodes (OLEDs) is very well known and has been extremely successful for developing low-voltage-driven light-emitting devices, eventually fabricated on large-area flexible substrates. However, since OLED is a current-driven device,

its application, for example, in display technology, requires high-quality TFT backplanes such as those based on LTPS—Low-Temperature Polysilicon—which increase, on the one hand, the production costs and, on the other hand, hinder the development of a truly flexible platform. On the contrary, OLET is a voltage-driven device that can be switched on and off exclusively by applying a potential, with no constraints on the current density of the switching device. This has the profound implication that lower quality TFT backplanes can be used to drive OLET frontplanes in a radically new approach toward low-cost and flexible display technology. In addition, the combination of electrical switching and light generation in a single device structure simplifies the driving circuit of the display, and therefore the manufacturing processing, ultimately leading to decreased production costs. It is also worth mentioning that OLETs offer an ideal structure for improving the lifetime and efficiency of organic light-emitting materials due to the different driving conditions with respect to standard OLED architectures and to optimized charge carrier balances.

This book aims at providing the scientific fundamentals and the key technological figures of organic light-emitting transistors (OLETs) by putting them in the context of organic electronics and benchmarking their characteristics with respect to OLEDs for applications in display and sensing technology.

In chapter 2, the OLED device features and its state-of-the-art performances are reviewed and the display technology applications are discussed. A comparative analysis of the OLED with respect to the OLET is provided to highlight the fundamental differences in terms of device architecture and working principles.

In chapter 3, the basic optoelectronic characteristics of OLETs are reported and the different structures of the active layer are correlated to the device properties.

In chapter 4, the constituting building blocks of the OLET device are discussed and their role in determining the ultimate device performance is highlighted.

In chapter 5, the charge transport and photophysical properties of OLET are analyzed, with particular emphasis on the excitonic properties and the spatial emitting characteristics.

In chapter 6, the photonic properties of OLETs are presented, focusing on the external quantum efficiency, the brightness, and the light outcoupling and emission directionality and reviewing the opportunity offered by the OLET structure for the long-sought organic injection lasing.

In chapter 7, the key applications of OLETs are discussed, driving the attention to the potential impact on display technology and sensing.

2

ORGANIC LIGHT-EMITTING DIODES

When considering devices for achieving efficient and bright electroluminescence from organic materials, it is mandatory to start any analysis from organic light-emitting diodes (OLEDs), which are by far the most advanced and developed organic electroluminescent devices. OLEDs are successfully tackling the mobile display market and are gaining momentum for general lighting applications. In this chapter, the characteristics of OLEDs in terms of device structure and working principle are outlined and the main applications of the OLED technology reviewed. By directly comparing the vertical diode architecture with the planar transistor structure, it will be clear that organic light-emitting transistors have the potential to enhance the optoelectronic performances of the photonic components, while preserving the simplicity of the system architecture at potentially lower production costs. Indeed, the combination of electronic, optoelectronic, and photonic functionalities in a single device structure has the potential to pave the way toward a novel technological platform with high integration capability and simplified manufacturing process.

2.1 OLED DEVICE STRUCTURE AND WORKING PRINCIPLES

OLED displays possess a number of advantages over conventional display devices, such as high brightness and contrast, high luminous efficiency, fast response time, wide viewing angle, low power consumption, and lightweight.

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Although manufacturing costs are an issue, OLED displays can be fabricated on large-area substrates (including flexible substrates) and offer a virtually unlimited choice of colors. The technological promise of these unique characteristics puts OLEDs at the forefront of research efforts by a number of government agencies, industries, and universities. Major industrial electronics players and a number of newcomers have invested heavily in OLED research and development. As a result, a stream of new OLED products has reached the marketplace and a number of large-scale manufacturing facilities have been built or are under construction. Although the field is expected to continue growing at a rapid pace, major challenges still remain, especially the lack of highly efficient and stable organic light-emitting materials, the critical operational lifetime of the blue color, and technical hurdles in large-scale manufacturing yields of the OLED displays.

In general, light-emitting diodes (LEDs) are optoelectronic devices, which generate light when they are electrically biased in the forward direction. The early commercial LED devices, in the 1960s, were based on inorganic semiconductors such as gallium arsenide phosphide (GaAsP) as an emitter, and their efficiencies were very low. After 40 years of development, the efficiencies of inorganic LEDs have been significantly improved, and they are used in a wide range of applications such as telecommunications, indicator lights, and solid-state lightening. For flat-panel displays, the applications of LEDs have been limited to billboard displays where individual LEDs are mounted on the display boards.

Once organic thin films (either small molecules or polymers) are implemented in the diode active layer, the device is named OLED. Before the realization of the first OLED, organic-based devices could be operated only in electroluminescence mode. The first organic electroluminescence device was demonstrated in the 1950s, and very high operating voltages were required. These devices were made of anthracene single crystals doped with tetracene, which were inserted between two metal electrodes. Very high driving voltages were required and the efficiencies were very low. In the 1980s, a technological breakthrough was achieved by lowering the turn-on voltage in OLEDs. Indeed, OLEDs based on multilayer active region were fabricated consisting of a transparent anode, a hole-transporting layer, an electron-emitting layer, and a cathode. During the operation, electrons and holes are injected from the cathode and the anode, respectively, which then recombine radiatively generating light. The operation of OLEDs is similar to that of LEDs.

OLEDs are ultrathin, large-area light sources made of thin-film organic semiconductors sandwiched between two electrodes. State-of-the-art small-molecule-based OLEDs consist of various layers—each layer having a distinct functionality. These films are prepared by thermal evaporation in high

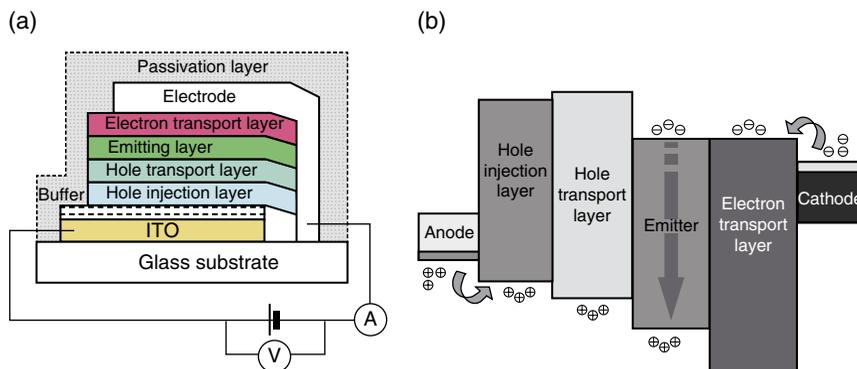


FIGURE 2.1 Multilayer OLED device structure (a) and working principle (b).

vacuum or organic vapor-phase deposition [1–3]. In contrast, polymer OLEDs are typically processed by spin-on or spray-coating techniques [4,5], where the solvent is removed by annealing steps. Polymer OLEDs are limited in their complexity owing to the fact that the solvents used often harm the underlying layers. In order to improve the general complexity of wet-processed devices, significant effort is spent on improving polymer processing.

The general architecture of an OLED, in the case of conventional bottom-emitting device, comprises a transparent electrode on top of a glass substrate (anode), followed by one or more layers of organic materials and capped with a highly reflective metal electrode (cathode). By altering the optical properties of the electrodes, top-emitting [6–8] and transparent [9] OLEDs can be fabricated. The schematic representation of a device structure and the energy level diagram of a typical multilayer OLED is reported in Figure 2.1. Firstly, efficient hole injection from the anode and efficient electron injection from the cathode are mandatory for obtaining high-efficiency devices. In inorganic semiconductors, carrier injection is achieved by heavily doping the semiconductors (n- or p-type) at the contacts to allow tunneling of the carriers through the barriers. In organic semiconductors, the optimization of injection process is obtained by matching the work-function level of the anode metal with the highest occupied molecular orbital (HOMO) of the organic semiconductor for hole injection and the work-function level of the cathode metal with the lowest unoccupied molecular orbital (LUMO) of the organic semiconductor for electron injection. The most commonly used metals and conductive oxides present work-function levels that are well aligned with the HOMO levels of the organic materials, while highly reactive low work-function metals are generally required for electron injection electrodes. To facilitate carrier injection upon the application of the external electric field,

carrier injection layers with proper energy alignment with injection electrodes are necessary. Specifically, an electron injection layer (EIL) with the LUMO level matching the work-function level of the cathode is needed, while a hole injection layer (HIL) with its HOMO level matching the work-function level of the (transparent) anode is needed. To transport the injected carriers from the injection layer to the emitting layer, electron-transport layer and hole-transport layer are necessary (ETL and HTL, respectively). The migration of charge carriers (or polarons as the charge carriers are referred to when placed into a highly polarizable medium such as organic materials) occurs by means of a so-called *charge-hopping mechanism* [10] through the electron- and hole-transport materials. Ideally, the electron-transport layer should have high electron bulk mobility and the HTL should have high hole bulk mobility. In addition, these transport layers have a large energy gap in order to provide an energetically favored path for one type of charge carrier, while acting as a blocking layer for the other charge carrier. The energy level diagram of the overall system has to be designed such that the HTL presents a wide energy gap and the HOMO level matches the HOMO level of the HIL. In such configurations (Figure 2.1b), the LUMO level of the HTL is higher than the LUMO level of the ETL with the consequent formation of an energy barrier for the transport of the electrons.

The energetic constraint inherently related to the heterostructure approach is functional to the efficient light formation into the device. Indeed, the charges are favored to gather in the emission layer (EML) and recombine, an exciton is formed, and depending upon the nature of the emission materials and according to appropriate selection rules, singlet fluorescence or triplet phosphorescence is emitted. Although the structure of a typical OLED may contain many layers, not all of these layers are necessarily present in all OLED architectures. As it can be easily understood, much of the current research on OLEDs focuses on the development of the simplest possible and most easily processed architecture that can deliver the optimal combination of device properties.

Let us consider in more detail the specific characteristics required for the organic materials comprising the most important functional layers.

The HTL materials are very common in small-molecule-based OLED devices but are less common in polymer-based devices because conjugated polymers are usually good hole conductors themselves. They serve to provide a hole-conductive (via charge hopping) pathway for positive charge carriers to migrate from the anode into the EML. On the basis of this requirement, hole-transport materials are usually easily oxidized and are fairly stable in the one-electron oxidized form. This feature is related to the shallow HOMO energy level in the solid state, which is preferably isoenergetic with the

anode/HIL workfunction and lower in energy than the HOMO energy level of the EML. This latter property improves the chances of charge flow into the EML with minimal charge trapping. As the main function of the HTL is to conduct the positive charge carrier holes, hole traps (higher energy HOMO materials) should be avoided either in the bulk of the material (i.e., hole-trapping impurity levels $\ll 0.1\%$ are typically required) or at interfaces. Another function of the HTL is that it should act as an electron-blocking layer to prevent the flow of electrons from the EML and ultimately to the anode. For this purpose, a very shallow LUMO level is desirable.

Materials having low ionization potential together with low electron affinities and high hole mobility usually function as hole-transporting materials by accepting and transporting hole carriers. The most common hole-transport materials are *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,10-biphenyl-4,40-diamine (TPD), *N,N'*-diphenyl-*N,N'*-bis(1-naphthylphenyl)-1,10-biphenyl-4,40-diamine (NPB), and 1,10-bis(di-4-tolylaminophenyl)cyclohexane (TAPC). Ongoing efforts on the development of HTLs include the improvement of thermal and electrochemical stability, mobility, glass transition temperature, and reduction in the energy barrier interface between the anode and HTL and the crystallization behavior.

The ETL functions as a conducting material to help transport electrons from the cathode and into the organic layers of the device—ideally, transporting the electrons via a hopping mechanism involves transitory production of anion radicals (negative polarons) in the molecules involved. As such, the material needs to have a LUMO level close in energy to the work function of the cathode material used so as to aid charge injection. It also needs to be comprised of a material that is relatively stable in its one-electron reduced form. As with all organic layers, it should form good amorphous films and have a high transition temperature to favor stable operation over extended periods.

Since most of the high-efficiency organic emitters have p-type character and mainly hole-transporting behavior, to achieve high efficiency device performance an electron-transport layer is necessary to balance the charge injection and transport. In fact, it is documented that introducing an ETL into OLEDs results in orders of magnitude improvement in the device performance. The functions of the ETLs are to reduce the energy barrier between the cathode and the emitter and to help the electrons to be easily transported to the emitter. The introduction of an ETL lowers the energy barrier between the LUMO level of the EML and the work function of the cathode for electron injection. Meanwhile, most ETLs also serve as hole-blocking layers to efficiently confine the exciton formation in the EML and thus balance charge injection. It also prevents the charge leakage and the accumulation of charges at the cathode and ETL interface.

Materials having good electron-transporting and hole-blocking properties (i.e., electron mobility higher than 10^{-5} cm²/Vs) and high electron affinities together with high ionization potentials are the favorite materials for accepting negative charges and allowing them to move through the molecules. The most common ETL materials are aluminum-tris-8-hydroxyquinoline (Alq₃) and 9,10-di(2-naphthyl)anthracene (ADN).

Finally, let us consider in more detail the EML, which is considered the distinctive layer in an OLED device. Indeed, the major part of the molecular design and engineering of materials comprising OLEDs is devoted to the emissive materials. In many cases, however, the EML is actually a mixture of two or more materials wherein there is at least one electroluminescent emissive material coupled with a charge-transporting host material. Such guest–host systems are extremely common in OLEDs based on small molecules (SMOLEDs, small-molecule organic light-emitting diodes), whereas in polymeric OLED devices, the emitter layer is usually composed of a single polymer (PLEDs, polymer light-emitting diodes), which combines both the light formation and charge-transport functionalities into a single-phase material. Clearly, this is a broad generalization given that it is possible to use a single material for the emitter layer in SMOLEDs and multiple-phase layers (e.g., polymer blends or doped polymers) in polymeric OLEDs.

In general, SMOLEDs contain small-molecule emissive materials that can be processed by either vacuum deposition techniques or solution coating. The emissive small molecule may be a fluorescent (singlet excited state) or a phosphorescent (triplet excited state) emitter.

PLEDs contain polymeric emissive materials that are almost exclusively processed by solution coating. In general, fluorescent emission is observed in PLEDs, but there are only few examples of phosphorescent materials being incorporated into a polymer chain and used as phosphorescent emitters.

In spite of technological issues of efficiency and stability of PLEDs as compared to SMOLEDs, the former promises to revolutionize the display-manufacturing technology as it provides the possibility of inexpensive solution fabrication.

Indeed, ambient temperature and pressure fabrication conditions (spin coating, bar coating, inkjet printing, etc.) of PLED-based large-area screens, enabled by good film-forming properties of polymers, are particularly attractive for the industrial application. However, purely polymer-based LEDs present external quantum efficiency (EQE) of less than 10%, which limits the achieved power efficiency below ~20 lm/W. Besides the energy consumption issue, low efficiency also poses a problem of heat dissipation, which affects the device stability.

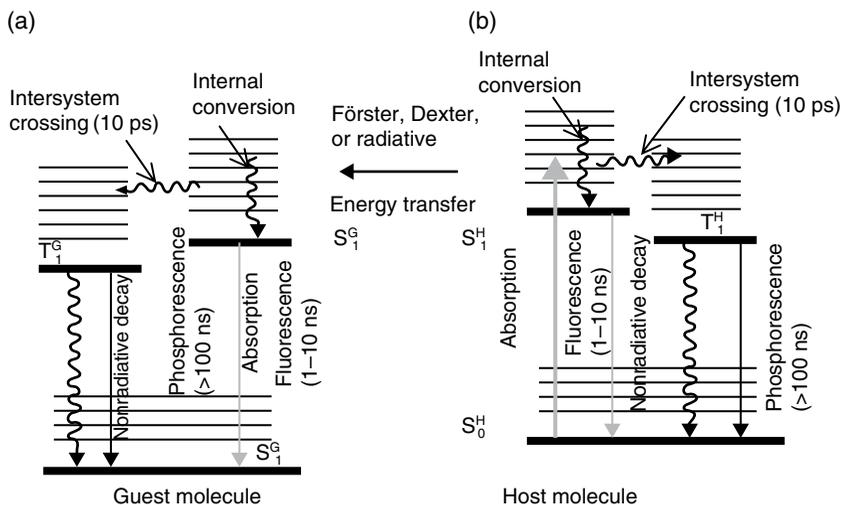


FIGURE 2.2 (a, b) Electronic processes of host-guest molecules, in which the guest molecules can emit light through both singlet and triplet states. S_0^H, S_0^G : a singlet ground state of the host and guest molecules, respectively. S_1^H, S_1^G : a first excited singlet state of the host and guest molecules, respectively. T_1^H, T_1^G : a first excited triplet state of the host and guest molecules, respectively.

In such highly complex, multilayer, and multicomponent OLED devices, a successful strategy to effectively master the distribution of the excitation in the desired emitting molecules is to manage the dynamics of the various energy-transfer mechanisms taking place in the luminescent active layers. When a host molecule in the typical host-guest EML is excited from the ground state by either absorbing light energy or being driven by electric energy to a higher vibrational energy level, it is subjected to collisions with the surrounding molecules. It can directly release its energy through radiative decay or nonradiative decay processes to the ground state, or in the presence of a suitable guest molecule, energy-transfer processes may occur. The latter event, depicted in (a) of the diagram reported in Figure 2.2 as an energy-transfer transition from the host molecule to the guest molecule, occurs through Förster, Dexter, or radiative energy-transfer processes. At this point, the radiative decay processes will occur from the luminescent guest molecules. It may be noted that the emission spectrum observed is sometimes the emission from the guest molecules only due to complete energy-transfer processes, but sometimes it combines the guest and host molecule emission due to incomplete energy transfer (Figure 2.2).

Because molecular excited states may also transfer from molecule to molecule while conserving their spin and energy, one can treat them as quasiparticles

named excitons. The highly localized excited states are known as Frenkel excitons, having radii of a few angstroms.

One can treat the Frenkel exciton formation as due to the hop of charge carriers (electron, hole) to a neighboring molecule. Due to the fact that the rate of exciton hopping is given by the multiplication between the rate of electron transfer and the rate of hole transfer, the theory of electron transfer can shed light on the understanding of exciton hopping.

During OLED operation, singlet and, in some cases, triplet excitations may first be created in the host material. Then, through charge or energy transfer from the host to the guest, singlet or triplet excited states are formed in the guest. For an effective host-guest system, several factors have to be considered, such as the phase compatibility of the host and guest, the aggregation of the molecules, and the host-guest energy level alignment.

In this charge/energy-transfer process, the band gap of the guest should fall within the band gap of the host to favor transport of electrons and holes from the host to the guest, where they should then recombine (Figure 2.2). In order to dominate efficient energy-transfer process requires that the energy of the excited state of the host should be higher than that of the emissive excited state of the guest. This applies to both singlet excited states and triplet excited states of the host and the guest as shown in Figure 2.2.

The efficiency of energy transfer for the singlet excited (fluorescent) state is easy to verify if there is an overlap between the emission spectrum of the host and the absorption spectrum of the guest. Beyond this requirement, for an efficient energy transfer from the host to the guest of the triplet state (phosphorescent), the excited triplet state of the host should be higher than that of the guest.

Finally, we have to mention the other photophysical mechanism, which is typically used for localizing the excitons on the guest molecules. In the *charge-trapping* process, a hole (electron) generated in the host during device operation is directly localized on the guest molecule if the HOMO (LUMO) of the guest lies above (below) that of the host material. Then, the counterparticle is trapped on the guest energy well, thus forming an exciton. The higher the difference between the HOMO (LUMO) levels of the host and the guest, the higher is the efficiency of hole (electron) trapping, and sometimes, direct charge trapping could be the prime mechanism of the exciton generation on the guest molecules. However, the charge trapping also creates a barrier for charge transport across the device, resulting in significant increase of the operating voltage.

In general, the approach of engineering the active stack in the EML is fundamental in improving the internal efficiency of OLEDs. Indeed, the

majority of organic semiconductors form amorphous, disordered films [10]. As a consequence, charges are injected statistically with respect to their electron spin, finally determining the formation of singlet and triplet excited states. Because the triplet state has a multiplicity of 3 [10], on average 75% of the excitons formed are triplet states, with the remaining 25% being singlets. Segal *et al.* [11] observed slightly smaller values for the singlet fraction in both small-molecule and polymeric systems [(20% ± 1%) and (20% ± 4%), respectively], which are in rather good agreement with this simple statistical picture.

The low singlet fraction causes OLEDs based on fluorescent emitter molecules to be rather inefficient with an upper limit of the internal quantum efficiency $\eta_{\text{int}} = 25\%$, because emission solely occurs in its singlet manifold.

Several routes have been proposed to obtain a higher η_{int} through the efficient harvesting of excitons in OLEDs, in particular triplet excitons. Historically, the very first experiments with ketone derivatives which showed intense phosphorescence at low temperature opened a new method for triplet harvesting even though the EQE (η_{EQE}) was limited to a low value [12]. Rare metal complexes containing Eu and Tb established intramolecular cascade energy transfer as another route to harvest triplet excitons but did not show promising η_{EQE} [13–15]. Later, a successful strategy was realized using room-temperature phosphorescent emitters such as platinum and iridium complexes. In this case, following the mixing of the spin orbitals of S_1 and T_1 states due to the presence of a heavy atom, the radiative decay rate from the T_1 state to the ground state is significantly improved.

Along with realizing a highly efficient emissive triplet state in a molecule, the heavy-metal effect strongly enhances the intersystem crossing rates between the singlet and triplet manifolds [16]. Thus, the fractions of singlet excitons that are created under electrical excitation are efficiently converted into triplet states before they can recombine radiatively. The intersystem crossing rate is close to unity in various phosphorescent systems [17]. Therefore, phosphorescent materials in OLEDs can lead to internal EL efficiencies of $\eta_{\text{int}} = 100\%$.

Furthermore, state-of-the-art emitters are especially optimized for having short excited-state lifetimes in order to reduce bimolecular quenching processes, which limit the photoluminescence quantum yield at high excitation levels [18,19].

In addition, the utilization of phosphorescence emitters as a triplet sensitizer has been proposed [11,12]. Using this process, triplet harvesting realized by energy transfer from the T_1 state of a phosphorescent emitter such as an iridium 2-phenylpyridine complex to the S_1 state of a fluorescent emitter via dipole–dipole coupling (i.e., Förster energy transfer) resulted in an

$\eta_{\text{int}} = 45\%$ [20]. However, the rather limited η_{int} is due to the presence of the competitive deactivation process of triplet–triplet energy transfer.

Although OLEDs based on fluorescent molecules, which are composed of simple aromatic compounds, have continued to attract interest because of their longer operational lifetimes in the blue-emitting range, higher color purity (narrow spectral width) EL, and broader freedom of molecular design compared with phosphorescence-based OLEDs [21–23], the η_{int} of traditional fluorescence-based OLEDs is limited to less than 25% even in the ideal case. Therefore, the enhancement of η_{int} in OLEDs using conventional fluorescence-based emitters is still obviously a major concern for the development of future OLEDs.

A concept to improve the internal quantum efficiency of fluorescent EL makes use of the high triplet density via delayed fluorescence [10]. Here, the interaction of two triplet states (called triplet–triplet annihilation) will create delayed singlet excitons: $T_1 + T_1 \rightarrow S_0 + S_n$ [24]. Based on this nonlinear process, an internal electron–photon conversion efficiency much higher than expected is reached. The device data of Okumoto *et al.* [25] showing a twofold improvement to the $\eta_{\text{int}} = 25\%$ limit (nearly 10% EQE) suggest that this process takes place.

Kondakov [26] gave experimental evidence that delayed fluorescence substantially contributes to the internal efficiency of fluorescent OLEDs. Endo *et al.* [27] suggested an alternative concept [thermally activated delayed fluorescence (TADF)] to feed the singlet state of a molecule with its triplet excitons.

The typical energy diagram of a conventional organic molecule, depicting singlet (S_1) and triplet (T_1) excited states and a ground state (S_0) is reported in Figure 2.3 [28]. In standard state-of-the-art phosphorescent systems, the S_1 level is considerably higher in energy than the T_1 level, by 0.5–1.0 eV, because of the electron exchange energy between these levels (Figure 2.3). However, a careful design of organic molecules can lead to a small energy gap (ΔE_{ST}) between S_1 and T_1 levels. Correspondingly, a molecule with efficient TADF requires a very small ΔE_{ST} between its S_1 and T_1 excited states, which enhances $T_1 \rightarrow S_1$ reverse intersystem crossing (RISC). Such excited states are attainable by intramolecular charge transfer within systems containing spatially separated donor and acceptor moieties [28]. The critical point of this molecular design is the combination of a small ΔE_{ST} of ~ 100 meV with a reasonable radiative decay rate, to overcome competitive nonradiative decay pathways, leading to highly luminescent TADF materials. Because these two properties conflict with each other, the overlap of the HOMO and the LUMO needs to be carefully balanced. Furthermore, to enhance the photoluminescence efficiency of a TADF material, the geometrical change in molecular

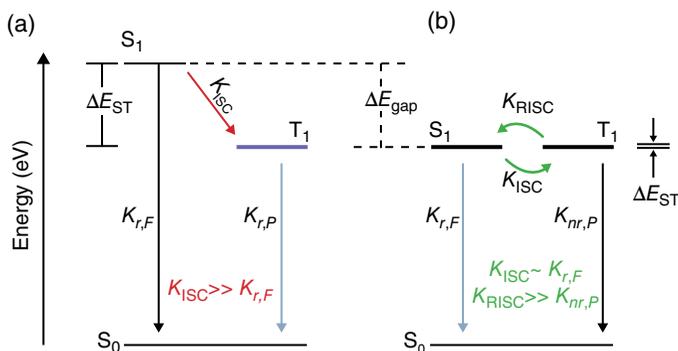


FIGURE 2.3 Comparison between the (simplified) energy level diagram for standard phosphorescent (a) and TADF-based (b) emitters. Important rates k_i are indicated. *r*, radiative; *nr*, nonradiative; *F*, fluorescence; *P*, phosphorescence; ISC, intersystem crossing; RISC, reverse ISC; ΔE_{ST} , singlet–triplet splitting. [Source: Reineke [28], Figure 1, p. 269. Adapted with permission from the Nature Publishing Group.]

conformation between its S_0 and S_1 states should be restrained to suppress nonradiative decay. The RISC rate (k_{RISC}) (Figure 2.3), which is the rate-limiting step in TADF emitters, has been demonstrated to be as high as 10^6 s^{-1} . As shown in Figure 2.3, state-of-the-art phosphorescent molecules possess radiative rate constants of the same order of magnitude.

Devices based on this concept showed a very high RISC efficiency of 86.5% and an EQE beyond the fluorescence limit of 5%. Recently, Uoyama *et al.* [29] reported promising OLED performance data based on this TADF concept. With a specially designed novel class of organic materials, the exchange splitting could be reduced to approximately 80 meV, giving rise to an effective RISC. These materials possess a very high rate of delayed fluorescence, which is comparable to the radiative rates of phosphorescent emitters [30]. In their report, OLEDs are discussed reaching 19% η_{EQE} , which is in line with the currently used phosphorescent emitter technology. It is expected that TADF will potentially allow internal quantum efficiencies of light emission of 100%, similarly to phosphorescence allowing for the development of truly spin-indifferent organic LEDs.

Although the scientific community is actively pursuing research into this typology of materials, the industry may be reluctant to embrace TADF-based OLED concept immediately. At the production level, existing OLED products have resulted from years of development and radical new designs introduce risk, substantial investment, and facility downtime. The lower cost of TADF emitter synthesis relative to the high cost of transition metals such as iridium

may alone be insufficient to persuade the industry to make a technology switch. However, if TADF does lead to blue OLEDs with considerably superior stability compared to phosphorescence, the industry is likely to consider adopting it.

We have also to mention that Segal *et al.* [31] introduced the mixing of charge-transfer (CT) states in small-molecule host-guest system for enhancing the emission from fluorescent material (extrafluorescence). By assuming that exciton formation follows the relaxation of a CT state consisting of an electron and a hole on neighboring molecules, the anomalous higher lying triplet CT state can be exploited for increasing the rates of singlet exciton formation, leading to a singlet fraction as high as $\chi_S=0.84\pm 0.03$ [31].

Aside from the optimization of the device multistack architecture and the photophysical processes ruling the light formation, a major limiting factor in terms of efficiency is the outcoupling of light [32]. Since a standard OLED consists of a highly reflective cathode on one end and a semitransparent anode on the opposite end, it essentially forms a microcavity where certain modes (or wavelengths) of light are enhanced whereas other modes are trapped inside, depending on the total device layer thickness [33]. This is related to the fact that standard organic materials as well as the indium tin oxide (ITO) in the anode have higher refractive index values ($\sim 1.7\text{--}1.9$) than those of the glass substrate (~ 1.51) and air. This results in even more modes of light being trapped in the high refractive index layers in the device due to internal total reflection and consequentially leads to a directional (angular-dependent) emission profile [34].

We consider in more detail the various light propagation modes in a conventional bottom-emission OLED (see the device cross section reported in Figure 2.4). They are mainly determined by the thin-film structure of the device and the respective optical properties (i.e., refractive indices and absorption coefficients) [38].

In general, the generated photons can outcouple to an external light mode (the so-called far-field, air, or outcoupled modes) and leave the device through the transparent anode (ITO) and substrate (glass). This, however, is only accomplished by 20–30% of the photons generated within an emission angle cone of around 40° . The majority of the photons outcouple to either substrate modes in the glass or waveguide modes in the ITO and organic layers.

Coupling to organic or waveguide modes [35] (Figure 2.4) occurs when the photon path exceeds the critical angle of total internal reflection due to the large refractive-index mismatch between the organic layers, substrate, and air. In the first approximation, two optical interfaces, that is, the organic/substrate and the substrate/air interfaces, are formed, where total internal reflection may occur. Coupling reflects the photons back through the substrate

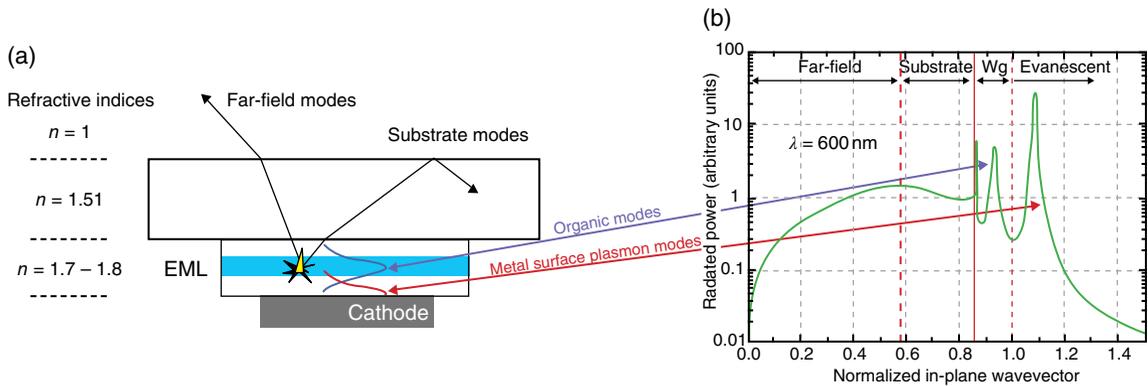


FIGURE 2.4 (a) Cross section of an OLED with indication of different light modes. (b) Typical power spectrum of the internally generated light shown as a function of the in-plane wavevector. Vertical lines separate the various possible light modes. Neither waveguide (wg) nor evanescent modes (thick line) can be accessed with external-light outcoupling techniques; thus, they dissipate within the layer structure. Model calculation [36] for a bottom-emitting device similar to devices discussed in Reference [37]. [Source: Reineke *et al.* [35], p. 1252. Adapted with permission from American Physical Society.]

and organic layers to the reflective cathode. The segmented path taken by the photons is well described by geometrical ray optics and results in traveling distances in the centimeter range.

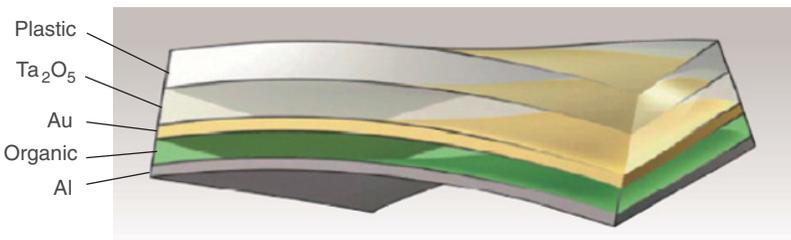
The waveguide modes trapped in the organic-transparent electrode layer system can be one of two types: either a zigzag mode that has a maximum in the organic layer or a plasmonic mode that propagates mainly along the highly reflective metal cathode and is therefore quickly absorbed [39–41]. Unfortunately, most of the photons that enter into a waveguide mode end up in the plasmonic mode given that this process is very efficient for short distances between the EML and the cathode.

Moreover, Figure 2.4 additionally shows a power spectrum, obtained from model calculations [36] of a conventional monochrome bottom-emitting OLED [32,42], plotted as a function of the in-plane wavevector [32,36,42]. In such a power spectrum, the modes discussed can easily be attributed to different ranges of the in-plane wavevector, indicated by the vertical lines in Figure 2.4. Here, the fraction of photons that directly leaves the device (far field) typically is in the range of only 20% [36,37,39,43,44]. More light can be extracted to the far field by applying modifications of the substrate/air interface by converting substrate into air modes [38,45–47,108]. On the contrary, as indicated by the thick solid line, modes with larger in-plane wavevector, that is, waveguide and evanescent surface plasmon modes, cannot be outcoupled by external techniques.

Different techniques in internal or external device modification are usually implemented in order to enhance light outcoupling efficiency in OLEDs. One common approach is to adopt thin-film outcoupling techniques by making use of refractive index modulation layers [48,49]. However, these techniques are typically effective for only a narrow range of emission wavelengths, sufficient for a single color OLED, but not for a white OLED with a broad-band emission spectrum.

Another popular approach is to use photonic periodic structures such as Bragg gratings [50,51] and low-index grids [46] in the device, which again only allows light management for certain modes of light. Moreover, these methods could not effectively address the issue of angular dependence in the emission profile. A more feasible outcoupling approach for OLED is to employ a buckling structure where a thick, corrugated architecture with a broad periodicity distribution persists throughout the entire OLED, such that a wide range of modes are enhanced and minimal angular dependence of the emission profile is present [52]. This technique can be readily combined with a number of cost-effective substrate surface texturing techniques such as the incorporation of an array of microlens [53] or micropyramids [47] to extract even more modes of light out of the device. Although this technique does

(a)



(b)



FIGURE 2.5 (a) Schematic of the OLED device structure on low-cost flexible plastic with metal electrodes. (b) Photograph of a large-area flexible OLED ($50 \times 50 \text{ mm}^2$) working at high luminance ($>5000 \text{ cd/m}^2$). [Source: Wang *et al.* [48], Figure 1, p. 754. Adapted with permission from Nature Publishing Group.]

improve outcoupling performance [35], it provides only a small enhancement to a mediocre OLED and is therefore incapable of reaching the efficiency levels attained by the best OLEDs.

The use of high-refractive-index substrates [47] that are better matched to that of ITO is also effective but less practical since high-refractive-index substrates are much more expensive than most commercial glass and flexible plastic substrates. Even though the plasmonic modes still exist but can be well suppressed, as recently shown for high-efficiency white OLEDs [54].

In particular, enhancements in optical outcoupling that rely on the use of high-refractive index layer is not recommended for low-cost mass production of OLEDs, which implement lightweight, flexible plastic substrates, because most plastics have a low refractive index ($n \leq 1.6$) that is comparable to standard glass. Thus, new optical outcoupling strategies are required to realize high-performance OLEDs on flexible plastic for the next generation of mass-produced flexible displays and solid-state lighting.

Wang *et al.* [48] presented a new paradigm for the optical outcoupling enhancement of OLEDs that is fully compatible with flexible plastic substrates with low refractive index. The key step of their technique is to replace the ITO transparent electrode with an oxide–metal–oxide electrode stack. They employed a multifunctional anode stack consisting of a thin semitransparent gold layer, which serves as a conductive electrode, sandwiched between a thin-film high-refractive-index layer made of tantalum oxide (Ta_2O_5) on a flexible plastic substrate—the optical coupling layer—and a hole-injection molybdenum trioxide organic layer. The gold layer forms a weak optical microcavity with the aluminum cathode. Because the design exploits a plastic substrate with a relatively low refractive index (<1.6), a high-refractive-index glass substrate is not required (Figure 2.5).

A record high EQE of $\sim 40\%$ at a very high brightness of $10,000 \text{ cd/m}^2$ was achieved using this new electrode design for a green OLED fabricated on flexible plastic (Figure 2.5). Additionally, after further reduction of the amount of light trapped in the plastic substrate using a lens-based structure on top of the device, the EQE and power efficiency at $10,000 \text{ cd/m}^2$ are increased to 60% and 126 lm/W , respectively.

2.2 APPLICATIONS OF OLED TECHNOLOGY

Tremendous progress has been made on OLEDs in the past two decades [47,48,54–58]. Since Kodak developed the first low-voltage OLED using a simple bilayer structure [59], Kido group [54] has demonstrated the first white OLED by mixing different colored emitters. Forrest's group [55] later

introduced phosphorescent emitters to quadruple the device efficiency by harvesting both singlet and triplet excitons through efficient intersystem crossing activated by the presence of the heavy metal in the emitter. Shortly after, Thompson's group [60] developed a platform for the synthesis of currently predominant Ir-based phosphors.

Recently, Leo group [47] reported an improved OLED structure, which reaches white fluorescent tube efficiency by combining a carefully engineered emitter layer with high-refractive-index substrates and using a periodic out-coupling structure. Particularly, it achieved a device power efficiency of 90 lm/W at 1000 Cd/m².

Indeed, OLEDs have high color quality and, as they can be made into large sheets, they can replace fluorescent lights that are currently used in houses and buildings with potentially reduced energy costs for lighting. Full-color capability is an essential feature in organic electroluminescent devices for flat-panel display. Moreover, OLED technology looks very promising for revolutionizing eco-sustainability in solid-state lighting in the next decade. This energy-efficient lighting technology may play an important role in reducing global consumption of electricity by almost 50%.

It is worth mentioning the synergetic strategy implemented by Leo group in order to engineer OLED devices capable of outperforming fluorescence tubes. The key feature of the white OLED layer structure is the positioning of the blue phosphor within the EML and its combination with a carefully chosen host material. Indeed, it is well known that for power-efficient white OLEDs, the high-energy blue phosphors demand host materials with even higher triplet energies to confine the excitation to the emitter [60]. Taking exciton binding energy and singlet–triplet splitting into account, the use of such host materials considerably increases the transport energy gap and therefore the operating voltage. For these reasons, blue fluorescent emitters are widely used to complete the residual phosphor-based emission spectrum [61,62]; this, as we have already said, either reduces the internal quantum efficiency or requires blue emitters with special properties.

A novel concept for achieving energy-efficient photon generation consists in locating the triplet energy level of the blue emitter material in resonance with its host so that the blue phosphorescence is not accompanied by internal triplet energy relaxation before emission. The exciton formation region is at the interface of a double-emission-layer structure [63] as reported in the energy level diagram of Figure 2.6. The blue host–guest system is surrounded by red and green sublayers of the EML to harvest unused excitons. Nonetheless, the different sublayers are separated by thin intrinsic interlayers of the corresponding host material to decouple the sublayers from unwanted energy transfer. In particular, the introduction of high-triplet-energy interlayer