Series in Display Science and Technology

In Byeong Kang
Chang Wook Han
Jae Kyeong Jeong *Editors*

Advanced Display Technology

Next Generation Self-Emitting Displays

Springer

Series in Display Science and Technology

The *Series in Display Science and Technology* provides a forum for research monographs and professional titles in the displays area, covering subjects including the following:

- optics, vision, color science and human factors relevant to display performance
- electronic imaging, image storage and manipulation
- display driving and power systems
- display materials and processing (substrates, TFTs, transparent conductors)
- flexible, bendable, foldable and rollable displays
- LCDs (fundamentals, materials, devices, fabrication)
- emissive displays including OLEDs
- low power and reflective displays (e-paper)
- 3D display technologies
- mobile displays, projection displays and headworn technologies
- display metrology, standards, characterisation
- display interaction, touchscreens and haptics
- energy usage, recycling and green issues

More information about this series at http://www.springer.com/series/15379

In Byeong Kang · Chang Wook Han ·
Jae Kyeong Jeong
Editors

Advanced Display Technology

Next Generation Self-Emitting Displays

Springer

Editors
In Byeong Kang
LG Display
Seoul, Korea (Republic of)

Chang Wook Han
LG Display
Seoul, Korea (Republic of)

Jae Kyeong Jeong
Department of Electronic Engineering
Hanyang University
Seoul, Korea (Republic of)

ISSN 2509-5900 ISSN 2509-5919 (electronic)
Series in Display Science and Technology
ISBN 978-981-33-6581-0 ISBN 978-981-33-6582-7 (eBook)
https://doi.org/10.1007/978-981-33-6582-7

© The Editor(s) (if applicable) and The Author(s), under exclusive license to Springer Nature Singapore Pte Ltd. 2021
This work is subject to copyright. All rights are solely and exclusively licensed by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.
The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.
The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, expressed or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This Springer imprint is published by the registered company Springer Nature Singapore Pte Ltd.
The registered company address is: 152 Beach Road, #21-01/04 Gateway East, Singapore 189721, Singapore

Contents

Phosphorescent OLEDs for Power-Efficient Displays 1
Tyler Fleetham and Michael S. Weaver

TADF and Hyperfluorescence 39
Junji Adachi and Hisashi Okada

Small Molecules in Ink Jet Printed OLEDs—History, Status, and Prospects 67
Sebastian Meyer, Manuel Hamburger, Sebastian Stolz, Miriam Engel, Anna Hayer, Hsin-Rong Tseng, Rouven Linge, and Rémi Anémian

Solution-Processible OLED Material: Based on Conjugated Polymer Technology 83
Takeshi Yamada

Chemical Mechanisms of Intrinsic Degradation of Emitting Layers in Organic Light-Emitting Devices 107
Youngmin You

Encapsulation Technology for Flexible OLEDs 129
Eun Gyo Jeong and Kyung Cheol Choi

Oxide Thin-Film Transistors for OLED Displays 151
Hyeon Joo Seul, Min Jae Kim, and Jae Kyeong Jeong

Pixel Circuits for OLED Displays 175
Kee Chan Park

Large-Size OLED TVs with White OLED 199
Chang Wook Han, Yoon Deok Han, Hyun Chul Choi, and In Byeong Kang

Quantum Dot-Enabled Displays 229
Charlie Hotz and Jeff Yurek

Electroluminescence Devices with Colloidal Quantum Dots 251
Seunghyun Rhee, Jeong Woo Park, and Wan Ki Bae

Micro-LED Technology for Display Applications 271
Dong-Seon Lee and Jang-Hwan Han

Display Techniques for Augmented Reality and Virtual Reality 307
Byoungho Lee and Youngjin Jo

About the Editors

In Byeong Kang received his B.S. and M.S. degrees in Electronic Engineering from Hanyang University, Seoul, Korea, in 1989 and 1991, respectively. He also received his Ph.D. degree in Electronic Engineering from the University of South Australia in 1998. He subsequently joined LG Display, Korea, as a engineer in 1991, where he worked on the design and characterization of display for various applications such as IT, TV, and Mobile. He served as CTO, executive vice president, in LG Display from 2014 to 2020, leading technology research and development of future flat panel display such as TFT-LCD, AMOLED, and flexible display. In particular, he has led development of rollable OLED TV, transparent signage OLED, and 8K UHD OLED TV. He has published more than 30 co-authored international journal papers and 130 international conferences. He has also presented many talks at major display conference including keynote speech. He is a fellow of The Society for Information Display. Now, he is also a regular member of The National Academy of Engineering of Korea.

Chang Wook Han is the head of OLED device technology department as a chief research fellow and a vice president in LG Display, Korea. He obtained his B.S. and M.S. degrees in Material Science from Seoul National University, Korea, in 1987 and in 1989, respectively. He also received Ph.D. degree in Electrical Engineering from Seoul National University, in 2007. The title of his Ph.D. thesis was "a-Si:H TFT and pixel structure for AMOLED on flexible metal substrates". Since joining LG Display in 1990, he has worked on the device and process development on a-Si:H TFT backplanes for AMLCD. He has also focused on enhancing the performance of OLED device and developing new OLED panel structure since 1999. In particular, he has led several projects that have developed tandem white OLED and encapsulation technology for TV. He has experienced the successful application of these technologies to the world's first 55-inch OLED TV and transparent OLED products. His research achievements were recognized and he was presented the LG Group's R&D Grand Award, in 2013. He has also developed the innovated white OLED devices to meet the requirement for 4K and 8K OLED TV. Recently, he is in charge of developing TADF, blue phosphorescence, self-emitting QLED, and cultivating new OLED device for AR/VR micro-display. He has published more than 16 authored international journal papers and 30 international patents on flat panel display. He has published 4 authored chapters of book. He has also presented over 20 talks at major display conference including invited talks. He has served The Society for Information Display and International Meeting on Information Display conference as a program committee member on OLED.

Jae Kyeong Jeong received his B.S., M.S., and Ph.D. degrees in material science and engineering from Seoul National University, Seoul, Korea, in 1997, 1999, and 2002, respectively. In 2003, he was a postdoctoral researcher at the University of Illinois at Urbana–Champaign. In 2004, he joined Samsung Mobile Display Corp. as a senior engineer, where he had focused on the design and development of Si and amorphous IGZO TFTs for AMOLED display. In 2008, he successfully developed the world's largest 12.1" Oxide TFT-driven AMOLED display as a project leader. In 2009, he joined Inha University Incheon, Korea, as an assistant professor, where he had continued the oxide semiconductor and related field-effect transistors. Since September 2015, he is with the Department of Electronic Engineering at Hanyang University as a professor. His research group is interested in next-generation display electronics, CMOS TFTs for IoT, stretchable electronics, and emerging semiconductor devices. He has published more than 163 authored (or co-authored) international journal papers and 112 international patents. His total citation number and h-index are 21,498 and 56, respectively, according to the latest scholar google search. Also, he is currently an editorial board member of Scientific Reports and Journal of Information Display.

Phosphorescent OLEDs for Power-Efficient Displays

Tyler Fleetham and Michael S. Weaver

1 Introduction

Over the past several decades, organic light-emitting devices (OLEDs) have transitioned from the lab to the marketplace and are now the leading technology for a wide range of display applications. OLEDs today can be manufactured at 8 K resolution [1], on a large scale, with remarkable efficiencies, color purity, and long lifetimes. Furthermore, many of the imaginative possibilities for OLED technologies have already found their way into commercial devices including foldable devices [2, 3], transparent displays [4], and rollable televisions [5]. These benefits and possibilities have led to their widespread adoption in a constantly growing number of markets including mobile displays, televisions, monitors, wearables, lighting, and more. While many technological developments have led to this success, none is more crucial than the development of highly efficient phosphorescent OLEDs (PHOLEDs). In this chapter, the physics and chemistry of phosphorescent emitters and their application in PHOLEDs will be discussed.

The first practical OLEDs, reported by Tang and VanSlyke in 1987, employed a heterojunction of an aryl amine hole transporting layer and the electron transporting complex tris(8-hydroxyquinolinato)aluminum (Alq_3), which also served as the fluorescent emissive material [6, 7]. This breakthrough demonstrated the utility of heterojunction interfaces in effectively confining charges enabling them to recombine to form excitons. Many further advances in device design helped improve the efficiency of charge recombination and further development of fluorescent materials improved the emission efficiency of the emitters. Ultimately, the efficiencies for fluorescent OLEDs were limited by the inability to harvest the triplet excitons which

---

T. Fleetham
305 Yardley-Newtown Rd., Yardley, PA 19067, USA

M. S. Weaver (✉)
23 Governors Lane, Princeton, NJ 08540, USA
e-mail: mikeweaver@oled.com

I. B. Kang et al. (eds.), *Advanced Display Technology*, Series in Display Science and Technology, https://doi.org/10.1007/978-981-33-6582-7_1

are generated in electroluminescent (EL) devices, limiting their internal electron to photon conversion efficiency $\eta_{\mathrm{int}} \leq 25\%$ [8]. In 1998, this limitation was overcome with the development of PHOLEDs which incorporated heavy metal organometallic compounds as dopants [9]. The incorporation of a heavy metal center such as Pt or Ir affords efficient harvesting of all the electrogenerated singlets and triplets and can emit efficiently from the lowest excited triplet state through the use of spin–orbit coupling (SOC) [10]. While this initial PHOLED report demonstrated only 4% external quantum efficiency (EQE), the principle of using heavy metal complexes to harvest 100% of the electrogenerated excitons energized the field and η_{int} approaching 100% were reported in just a few years [11]. In the more than two decades, since the first report of PHOLEDs, thousands of researchers have devoted their efforts to further improvement and discovery in this field leading to tens of thousands of published journal articles and patents. This large body of work has enabled extremely high EQEs exceeding 60% [12], operational lifetimes in the hundreds of thousands of hours, and OLEDs emitting across the spectrum from the ultraviolet to the infrared [13, 14].

2 Design of Highly Efficient OLED Devices

The efficiency of an OLED can be most completely described by the power efficacy (η) which is a measure of the perceived light per input power. This metric encompasses the power input, light emission, and the photopic response of the human eye and is given in units of lm/W. For a Lambertian emitting OLED source, the power efficacy for a Lambertian emitting OLED is given by

$$\eta = \eta_{l\mathrm{e}}\ \pi / V \tag{2.1}$$

where V is the operating voltage, and η_{le} is the luminance efficacy (in cd/A) given by the equation:

$$\eta_{l\mathrm{e}} = k\eta_{\mathrm{Int}} \cdot \eta_{\mathrm{Out}} \tag{2.2}$$

where η_{Int} is the internal quantum efficiency (% excitons to photons), η_{Out} is the outcoupling efficiency (a measure of how many generated photons are emitted from the device), and k is a constant depending on the photopic response of the human eye. Taken together the power efficacy can be described by

$$\eta = k\eta_{Int} \cdot \eta_{Out}\pi / V \tag{2.3}$$

This relationship highlights that to optimize device performance steps need to be taken to maximize the internal quantum efficiency, η_{Int}, and the light extraction efficiency, η_{Out}, and minimize the voltage, V.

Another common metric often reported in published results is the EQE (η_{EQE}) which is the percentage of photons emitted from the device per electron injected into the device.

$$\eta_{EQE} = \eta_{Int} \cdot \eta_{Out} \tag{2.4}$$

For the purposes of separating the analysis for the various steps in EL generation, η_{Int} can be expanded to be the product of photoluminescent quantum yield (PLQY, Φ), recombination efficiency, η_{r}, and the exciton utilization constant χ which is 0.25 for fluorescent materials and 1 for phosphorescent materials as a result of differences triplet harvesting discussed in Sect. 2.2.5. The resulting expression for EQE is

$$\eta_{EQE} = \chi \cdot \Phi \cdot \eta_r \cdot \eta_{Out} \tag{2.5}$$

2.1 Device Operation

An OLED consists of one or more organic layers 10–1000 s of nanometers thick between two electrodes. An electric field on the order of 10^6 Vcm^{-1} is then applied across the OLED in order to generate EL. To optimize the efficiency parameters mentioned above, it is important to consider each of the steps in converting injected charges into emitted photons. Figure 1 shows the process for generating electroluminescence from a typical OLED. Upon applying a voltage to the device, there is a series of five key processes that take place, namely: (1) charge injection, (2) charge transport, (3) exciton formation, (4) exciton decay, and (5) light extraction.

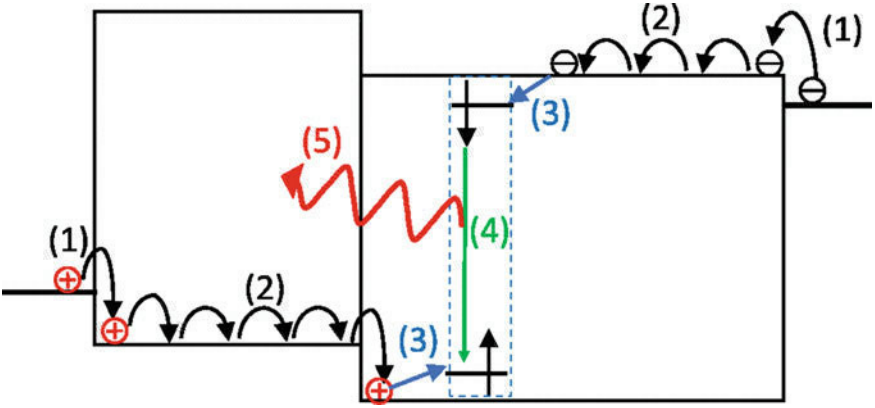

Fig. 1 Key processes in OLED device operation

(1) Charge injection: An electron is injected from the cathode to the lowest unoccupied molecular orbital (LUMO) of an organic molecule creating an anion. Similarly, an electron is removed from the highest unoccupied molecular orbital (HOMO) of an organic molecule by the anode creating a cation. While these charged species are formally organic molecules in their radical doublet states, it is often more convenient to describe them as “electron” and “hole” charge carriers, respectively, to borrow terminology from analogous charge transport processes in inorganic devices.

(2) Charge transport: Electrons and holes move through their respective transport layers under the influence of the applied electric field. In contrast to inorganic devices, these charge carriers are not free carriers, but rather oxidized or reduced molecules. The localized nature of these charged states requires that the charges must hop from the molecular orbitals of one molecule to the next via an intermolecular electron transfer. The spatial distribution in electron density of molecular orbitals, the barriers between potential wells of neighboring molecules, and the random orientation of the molecules in the amorphous film all slow this hopping process compared to charge transport in a crystalline inorganic solid [15]. As a result, the mobility of holes in typical organic materials is on the order of 10^{-3} $\text{cm}^2/(\text{V s})$ while electron mobility can be an order of magnitude or more lower [16, 17].

(3) Exciton formation: The electrons and holes are coulombically attracted and recombine in the emissive portion of the device to form a neutral excited state called an exciton[28]. This exciton is a bound excited state which is coulombically stabilized to prevent its dissociation back into free charge carriers. This recombination process generates a statistical mixture of 25% singlets and 75% triplets which for PHOLEDs all rapidly become triplets due to favorable intersystem crossing [18]. A more detailed description of this process follows in Sect. 2.2.5. Charge recombination can also form bimolecular or larger excited states extending over more than one molecule such as excimers [19] or exciplexes [20].

(4) Exciton decay: The exciton in its excited singlet or triplet state can relax to its ground state through either a radiative or non-radiative process. At room temperature, fluorescent materials only radiatively decay from their excited singlet state with a nanosecond lifetime [21]. Since 75% of the electrogenerated excitons are triplets, a large portion of the excited states are either lost through non-radiative pathways [8] or are upconverted back to the singlet state through a delayed fluorescence pathway [22, 23]. In the case of phosphors, all the excited states rapidly intersystem cross into the triplet state which can emit radiatively with a radiative decay lifetime in the microsecond time range [9]. These longer excited-state lifetimes allow for substantial exciton diffusion or other energy transfer processes before relaxing to the ground state.

(5) Light extraction: The photon generated in the exciton decay process is emitted from the OLED structure. Many photons are lost in this process due to a number of loss pathways including absorption processes in the organic stack or total internal reflection in the organic layers or substrate [24]. As a result of these

light extraction losses, and some losses from undesirable energy transfer events in the exciton decay process, in standard bottom emitting OLEDs less than 20–40% of the excited states created exit the device out of the front of the substrate [25, 26].

2.2 Components of an OLED Stack

The first organic EL devices attempted to create electroluminescence from single layers of organic material [27–29]. This required all the key steps to be optimized within a single layer. The organic heterojunction developed by Tang and Van Slyke afforded the ability to optimize the injection and transport of the holes and electrons separately [6]. Additionally, the barriers created by the heterojunction confined the recombination of charges to near the organic heterojunction interface. This ensured that a large proportion of the injected charges successfully formed an exciton and that this exciton recombination zone was far away from quenching interfaces at the electrodes. Further separation of the functions of charge injection, charge transport, and emission evolved toward the much more complicated device architectures used today which contain many layers [30–32], sometimes including layers of mixed compositions [33] to optimize each of the five key steps in generating efficient electroluminescence. The reason for this increased complexity is the limited capacity to tune the various properties of organic materials independently. It is often convenient to separate all the key steps in OLED operation into separate layers, each with a composition optimized for a specific role or small number of roles. As shown in Fig. 2, a typical device stack for modern OLEDs is depicted that will contain separate layers or materials for charge injection (HIL/EIL), charge transport (HTL/ETL), blocking layers to ensure efficient exciton formation (EBL/HBL), and an emissive layer (EML) optimized for efficient exciton formation and decay. Not depicted in Fig. 2 are the various light outcoupling strategies that will optimize the light extraction out of the device which will be discussed in Sect. 2.2.6. Despite the distribution of roles, it is important to consider the energetic and mobility differences between the layers to ensure the barriers to charge injection are low while also avoiding charge buildup at any interface. It is particularly important to consider the differences in electron and hole injection and transport. A large discrepancy between the delivery of charge carriers to the EML can lead to charge buildup and undesirable quenching or charge leakage effects [80]. Finding this balance can be challenging since the relative mobility of holes is typically an order of magnitude or larger than electrons in many common organic materials. Furthermore, ensuring this balance occurs across the entire range of practical driving conditions adds an additional layer of complexity with many devices showing reduced performances at very high or very low driving currents due to this imbalance [86].

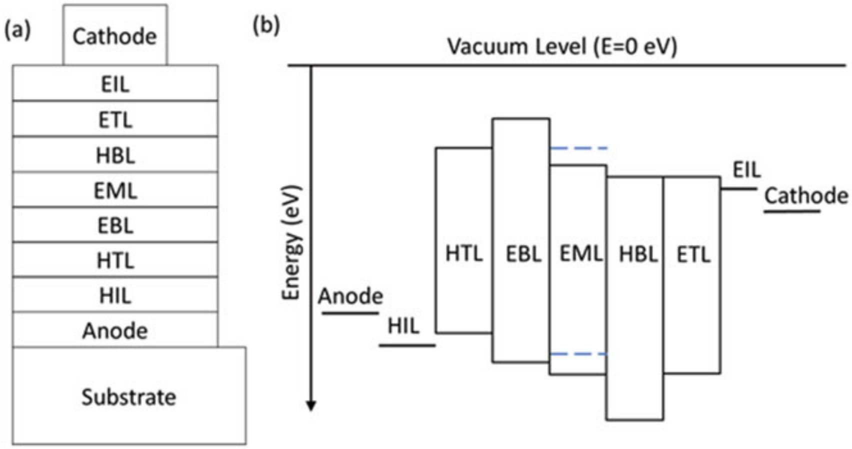

Fig. 2 **a** Typical OLED device stack and **b** schematic energy level diagram for state-of-the-art OLEDs where HIL is the hole injection layer, HTL is the hole transport layer, EBL is the electron blocking layer, EML is the emissive layer (which is typically doped with the emitter), HBL is the hole blocking layer, ETL is the electron transport layer, and EIL is the electron injection layer

2.2.1 Deposition of OLED Stacks

While the photophysical and electrochemical properties of each of the layers can be optimized independently, a common property among all the layers is the need to be compatible with the deposition technique and form high-quality, defect-free films. The most commonly used deposition technique is vacuum thermal evaporation (VTE), where organic layers are deposited sequentially onto the substrate from resistively heated source boats in a high-vacuum environment [34]. The organic material evaporation can take place from either the liquid or the solid state depending on the melting point and the temperatures required to reach an appreciable vapor pressure $> 10^{-3}$ Torr. For example, the hole transporting material, 4,4′-*bis*[*N*-(1-napthyl)-*N*-phenyl-amino] biphenyl (α-NPD), melts before evaporating under typical growth rates, whereas many of the other organic materials achieve a higher vapor pressure well before their melting point and evaporate via sublimation. The vacuum conditions under which OLEDs are fabricated are extremely important to the efficiency and operational stability of the devices so depositions are typically carried out in high vacuum at a base pressure of around 10^{-7}–10^{-8} Torr [35–37]. Evaporation rates of the organic materials are monitored using quartz oscillators and are typically in the range 0.01–0.5 nm/s in research and development tools. In large-scale manufacturing tools, higher deposition rates and longer times of continuous deposition from a source are required wherein the source is kept at elevated temperatures for 24–336 h. Therefore, materials must be able to withstand this environment without degradation which may reduce the quality of the deposited material or impact the ability to adequately access stable deposition conditions.

In order to maintain compatibility with the deposition requirements, there are several morphological and thermal considerations to be taken into account including molecular weight, morphological properties, sublimation temperature, decomposition temperature, and many others. Since small molecule organic materials must be able to be cleanly deposited by VTE without decomposing, selecting materials with moderate sublimation temperature in the range of 150 °C–450 °C and high decomposition temperature is important to ensure optimal device performance. Furthermore, during deposition, the material must form high-quality, defect-free films with precisely controlled thicknesses, typically in the region of 5–200 nm. The films must be stable for long periods and have a high glass transition temperature (T_g), e.g., $T_g > 110$ °C, to avoid crystallization over time [95, 96].

2.2.2 Electrodes

As mentioned in Sect. 2.1, the first key step in the operation of an OLED is the injection of charges into the organic layers. Making low resistance contacts requires optimal selection of the electrode materials with good conductivity, appropriate work function, high reflectivity (or transparency depending on the electrode), and deposition and patterning techniques compatible with the rest of the device stack. The anode for many OLED devices is typically indium–tin oxide (ITO) due it its good stability, transparency, and high conductivity. Several alternatives to ITO have been studied including polymers [38], metals [39], and other metal oxides [40]; however, ITO remains the present industry standard for bottom emitting devices (where light exits through the substrate) due to its favorable properties as well as its ability to be easily patterned using standard lithographic techniques to define different emitting regions or pixels on a substrate. Various deposition techniques and surface treatments have been studied to optimize the work function, conductivity, uniformity, and surface roughness of the ITO electrodes [41–44]. Treatment such as oxygen plasma or UV ozone exposure is particularly common since they lead to an enhanced device performance [42, 45], possibly due to the resulting increase in the work function of the ITO surface [43]. The exact stoichiometry of the ITO layer and the thickness can be fine-tuned for the required specifications of transparency, outcoupling constant, and conductivity. Typically, the ITO film is 50–200 nm thick and care has to be taken to minimize the surface roughness of the ITO layer to prevent shorts or nonuniform light emission from the thin organic layers. This can be particularly challenging in the case of flexible substrates and additional planarizing layers must be employed prior to deposition of the anode [46].

For bottom emitting OLEDs, the cathode contact should be highly reflective, have a low work function, and use a deposition technique that is compatible with organic layers underneath. Since the cathodes on standard bottom emitting devices are deposited on top of the organic layers care has to be taken to select materials, deposition rates, deposition source hardware, and patterning techniques which will not damage or contaminate the underlying organic layers. Aluminum is often the first choice as a cathode material chosen for its high reflectivity, moderate work function, and can be deposited relatively easily via VTE from resistively heated sources. Often, the cathode materials need to be used in conjunction with an electron injection material or alloyed with a low work function metal such as lithium, calcium, or magnesium in order to achieve an appropriate work function for efficient electron injection [47]. These materials are effective in tuning the work function of the electrode but these reactive metals are highly water and oxygen-sensitive which can make handling and processing challenging [48].

Other device structures such as top-emitting OLEDs or inverted OLEDs will employ different electrodes to satisfy the transparency and work function requirements of those devices. For top-emitting OLEDs the cathode is transparent allowing light to exit through the top of the device, while the anode is usually a highly reflective, high work function metal. Cathodes in top-emitting device architectures can be formed by using a thin metal contact [49], sometimes in conjunction with a conductive metal oxide [50], or a metal-free electrode [51]. The anode for a top-emitting OLED should have a high reflectance and a high work function such as Pt, Ag/ITO, or Al/Ni. If the anode is kept transparent, (e.g., ITO) in this top-emitting structure, the OLEDs can be made transparent and will emit light out of both sides of the device [52]. In an inverted structure, the cathode is in contact with the substrate and the organic stack is built up from the cathode interface to the anode in reverse order [53].

2.2.3 Hole Injection, Hole Transport, and Electron/Exciton Blocking Layers

The hole injection, hole transport, and electron blocking layers are collectively responsible for optimizing the delivery of holes to the EML while preventing the leakage of electrons to the anode where they avoid exciton formation. While these layers may not be directly involved with the emission of a photon, it is important to optimize these layers to reduce the driving voltage while preventing loss mechanisms such as hole trapping, exciton quenching at the EML interface, or electron leakage into these layers. Achieving optimal device performance requires an efficient injection into the HTLs, efficient hole transport through the layers and efficient injection into the EML. This multi-step process can be broken up into injection, transport, and blocking layers so that materials selection can be optimized separately for injection efficiency, high hole mobility, or suitable band offsets with other organic layers within the device. For more details on these processes, see Kalinowski [54] and Greenham and Friend [55].

Since the common anode material, ITO, has a work function < 5 eV [56] and the HOMO level of the hole conducting species in the EML can be as deep as −6 eV in blue OLEDs [57], it is important to make successive steps to ease the injection of holes into the EML or employ any strategies available to reduce this barrier. One strategy is the use of a hole injection layer which can serve several roles including modulate the work function of the anode, reduce the barrier to charge injection, planarize the substrate surface, and suppress recrystallization and delamination of the organic layer at the anode. Films such as copper phthalocyanine (CuPc) have been used to increase the adhesion of the HTLs and increase device lifetime [58], polymer layers such as poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) have been used to planarize the substrate surface to improve film uniformity [59], thin layers of carbon between the ITO and the HTL have been shown to decrease the operating voltage and improve the device characteristics [60], and thin fluorocarbon films on ITO have been used to enhance the stability of the anode interface [61]. Some of the largest performance enhancements from using hole injection materials come from the use of 1, 4, 5, 8, 9, 11-hexaazatriphenylene hexacarbonitrile (HATCN) (shown in Fig. 3) or MoO_3 because they have LUMO or conduction band levels close to the HOMO of common transport materials [62]. These extremely deep vacant energy levels allow these materials to freely remove electrons from the neighboring transport layer effectively doping the HTL with holes. In some cases, these materials have been codeposited to more strongly dope the hole transporting layer [63].

The primary layer for hole conduction is the HTL which is optimized for hole mobility. These materials typically contain electron-rich moieties which will readily accept holes from neighboring molecules or layers. Since charge transport occurs via hopping from the HOMO of one molecule to the next, hole transporting materials and their orientation in thin films should be designed to have enough orbital overlap between neighboring molecules to reduce the barrier for charge hopping. Various models have been proposed to describe charge transport in such materials [64, 65].

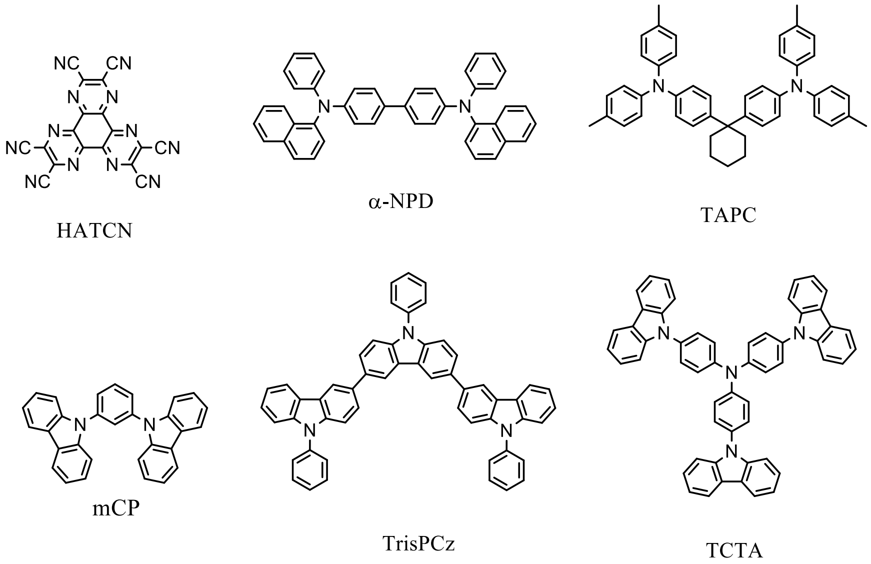

Fig. 3 Molecular structures of common hole injection, hole transporting, or electron/exciton blocking materials

One of the most common classes of material used are aryl-amines or carbazole-containing moieties, such as those shown in Fig. 3, which exhibit high hole mobilities [66, 67]. Furthermore, these materials have energy levels that are well aligned with the work function of ITO (>4.7 eV), giving a relatively small barrier to hole injection. α-NPD, for example, has a hole mobility of 10^{-3}–10^{-4} $cm^2/(V\ s)$ and a HOMO level of 5.4 eV [16]. While the hole mobility in these materials is already quite high, the drive voltage can be further reduced by conductivity doping of the HTL layers [68]. A green-emitting tris(2-phenylpyridine)iridium(III) ($Ir(ppy)_3$)-doped PHOLED device which used the tetrafluoro-tetracyanoquinodimethane (F_4-TCNQ) as a conductivity dopant in the HTL was observed to have a driving voltage 2.65 V to produce 100 cd/m^2 which is close to the minimum voltage possible to create a light emission of that energy [30]. This dopant achieves such a low voltage by removing electrons from the HOMO of the hole transport material to create charge carriers at a very low bias similar to the process described above for HATCN.

In order to achieve very high efficiencies, devices also typically contain an electron and/or exciton blocking layer (EBL). Such a layer requires particular attention paid to its energy levels more than the mobility. To control the exciton formation and emission processes, electrons should be blocked from entering the HTLs to ensure charge recombination occurs within close proximity to the desired emitter. Also, after exciton formation on the desired emitter, no nearby materials should have lower excited state energies which would serve as an exciton sink. In PHOLEDs, this means that the LUMO of the exciton blocker should be shallower (closer to vacuum) than the EML components and the triplet energy should be higher than the desired emitter. However, since only a thin layer is required to block electrons and the energy transfer radius is only a few nm, this layer can be kept sufficiently thin so the hole mobility is not as stringently important as in the thicker HTL. Conversely, since this blocking layer separates the HTL and the EML, there is more freedom in selecting an HTL material for high mobility without consideration of its triplet energy. Typically, an EBL can be achieved with molecules containing either carbazole or triarylamine moieties due to their hole mobilities and high bandgap, such as in 4,4′,4″-tris(N-carbazolyl)-triphenylamine (TCTA) [69], 9-Phenyl-3,6-bis(9-phenyl-9Hcarbazol-3-yl)-9H-carbazole (TrisPCz) [70], 1,3-Bis(N-carbazolyl)benzene (mCP) [71], or 1,1-Bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC) [68].

2.2.4 Electron Injection, Electron Transport, and Hole/Exciton Blocking Layers

The general design criteria for efficient electron transport are the same as those discussed above for hole transport, namely: good injection efficiency, high electron mobility, and suitable band offsets with other organic layers within the device. Similarly, electron transport can also be separated into injection, transport, and blocking layers to independently optimize the selection of the materials. One major difference between the hole transporting material selection and those for electron injection is

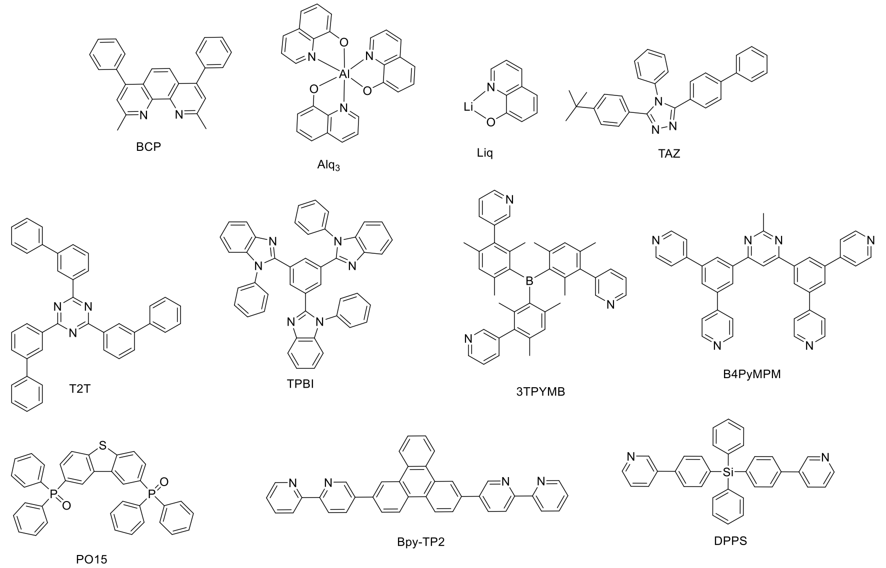

Fig. 4 Molecular structures of common electron injection, electron transporting, and hole/exciton blocking materials

the large barriers common for electron injection and that electron mobilities of most organic materials are orders of magnitude lower than those for holes.

The appropriate selection of an electron injection material will decrease the barrier between the work function of the cathode (>4 eV for metals like Ag and Al) and the LUMO of the electron-conducting material with the EML (often shallower than -2.5 eV). Lithium salts such as LiF [72] or complexes such as (8-hydroxyquinolinato)lithium (Liq) [73] (shown in Fig. 4) are also common as either thin electron injection layers or as conductivity dopants within the ETL to facilitate charge injection into the organic layers. It has been reported that LiF can reduce the work function for an Al electrode to 3.0 eV.

The primary layer for electron conduction is the electron transporting layer (ETL) which is optimized for electron mobility and also serves the function of being kept sufficiently thick to protect against defects introduced by the hot cathode deposition as well as prevent quenching of the emission by the plasmon modes from the cathode interface. These materials typically contain electron-deficient moieties such as aza-substituted aromatic rings, phosphine oxides [74], and boron-containing moieties, all of which will readily accept electrons from neighboring molecules or layers. Among the most commonly used ETL in OLEDs is Alq$_3$, as shown in Fig. 4 which has a LUMO energy level of 3 eV[16] and electron mobility of $\sim 5 \times 10^{-5}$ cm^2/(V s) [17]. More recently, several designs of electron-deficient molecules with large aromatic planes such as 2,4,6-tris(biphenyl-3-yl)-1,3,5-triazine (T2T) [75], 2,7-Bis(2,2′-bipyridin-5-yl)triphenylene (Bpy-TP2) [76], and 4,6-Bis(3,5-di(pyridin-4-yl)phenyl)-2-methylpyrimidine (B4PyMPM) [77] have demonstrated very high mobilities and improved device performance. In addition to selecting materials with high inherent mobilities, the ETL can be doped to further improve the mobility within the layer. One common class of material for this are organolithium complexes such as Liq [30].

In the region of the ETL that contacts the EML, it is common to use a hole and exciton blocking later to effectively confine the charges and excitons to the EML. Materials at this interface need to have several requirements: sufficient triplet energy to avoid quenching of the excitons in the device, good electron mobility and appropriate LUMO level to effectively inject electrons into the EML, and a deep (far from vacuum) HOMO level to prevent hole leakage into the ETL. One of the first materials used for this purpose is bathocuproine (BCP) which has a very deep HOMO level but a relatively low triplet [32]. Since then, several newly developed materials have been used as blocking layers including phosphine oxide-based materials such as dibenzo[b,d]thiophene-2,8-diylbis(diphenylphosphine oxide) (PO15) [74, 78], tetraphenylsilane materials such as diphenylbis(4-(pyridin-3-yl)phenyl)silane (DPPS) [79], boron derivatives such as tris(2,4,6-trimethyl-3-(pyridin-3-yl)phenyl)borane (3TPYMB) [80], or triazoles such as 3-([1,1′-biphenyl]-4-yl)-5-(4-(tert-butyl)phenyl)-4-phenyl-4H-1,2,4-triazole (TAZ) which are all good selections for this role due to their high triplets and deep HOMOs.

2.2.5 Emissive Layer

The emissive layer is largely responsible for the key performance metrics of internal quantum efficiency (IQE), color of emitted light, and intrinsic operational lifetime. In this crucial layer, the key steps of charge transport, exciton formation, and exciton decay must all be optimized simultaneously. EMLs can be comprised of either a neat layer of material or a mixture of two or more materials. While the former is appealing from a manufacturing perspective, the simultaneous optimization of all the key processes with a single organic or organometallic compound is extremely challenging. Furthermore, high concentrations or neat films of phosphorescent materials can lead to undesirable self-quenching effects such as triplet–triplet annihilation events or self-absorption that reduce the device efficiency [81]. As a result, most PHOLED EMLs are often comprised of a small amount of emissive material doped into a host matrix comprised of one or more host materials. In these doped layers, both the properties of the individual components of the EML and the compatibility of the various components need to be considered to optimize charge balance, reduce exciton quenching, and avoid emission contamination.

Charge Transport in Emissive Layers

Charge transport within the EML is primarily concerned with ensuring a balance of electron and hole transport so that the exciton formation occurs uniformly throughout the EML. A poor distribution of charges can lead to high concentrations of electrons or holes at an interface of the EML which in turn creates a concentrated exciton formation zone. High concentrations of charges and excitons can lead to bimolecular interactions such as triplet–polaron annihilation or triplet–triplet annihilation in which the excited triplet states are quenched by a neighboring charge or exciton reducing the internal quantum efficiency η_{Int} [82–84]. In order to avoid this efficiency loss it is important to select materials, and appropriate concentrations of the EML components that spread the exciton recombination zone across the EML. In a neat layer, achieving this balance would require the emissive material to have nearly identical hole and electron mobilities and would have no mechanism to ensure that the charges recombine.

An elegant solution to the problem of achieving charge balance is to dope the emissive material into an organic host matrix. This was first realized by Tang et al. by doping highly luminescent fluorescent dyes into a host matrix [31]. Since then, a wide range of fluorescent dopants has been used in OLEDs where the dopants can be used to easily alter the emission color, in addition to improving the efficiency and the lifetime of devices [85, 86]. In PHOLEDs, doping in an organic host effectively dilutes the concentration of the phosphorescent material preventing aggregation which can lead to an undesirable self-quenching effect [81]. If the excited state energy of the phosphor is lower than that of the host, any excitons formed in the host material will migrate to the dopant. Furthermore, since the relative ratio of host and dopant can be easily controlled in vapor-deposited devices achieving a charge-balanced device that optimizes the charge transport and exciton formation processes can be done with fine-tuning of the deposition rates of the EML components.

At low doping concentrations of the phosphorescent material, the majority of charge transport will occur on the host molecules [87]. In typical Ir(III)- or Pt(II)-based phosphors, the HOMO level is shallower (closer to vacuum) than that of the host material and can be considered a “hole-trap.” This trapping can slow down charge transport so particular care needs to be taken in the selection of the host materials to ensure that these traps are not too deep of an energetic well for the charges to get out (i.e., a host material should be selected with a HOMO close to that of the dopants). On the other hand, if the host energy levels are such that no charge trapping occurs, charges may transport too easily to the edges of the EML and lead to high concentrations of excitons and charges at those interfaces, which can reduce device performance. One strategy to achieve charge balance is to use a combination of host materials with electron and hole transporting capabilities. In this system, optimization of the relative concentration of the host components can effectively tune the charge balance so that the conduction of holes and electrons within the EML is approximately equal to avoid charge build up at either side of the EML [88]. However, if neither charge is trapped in these cohost systems, it is possible that both charges may transport easily through their separate domains to the opposite EML interface, so some degree of charge trapping is typically desired.

Once the concentration of the phosphorescent material is raised to ~3% the probability of the nearest neighbor being another dopant concentration increases and percolation pathways begin to form where charge transport can occur along with successive hops from dopant molecule to dopant molecule [89]. In typical phosphor systems at these doping concentrations, hole transport may occur primarily along these percolation pathways. One challenge in designing a balanced EML is ensuring that the charges can meet to eventually recombine. If both charges are carried through percolation pathways, it is possible that the charges may not come close enough for exciton formation to occur and the exciton formation process will be inefficient leading to losses in η_{Int} or increases in driving voltage. One strategy for achieving charge balance to improve device efficiencies and operational lifetime is using multiple EMLs of varying concentrations or using a gradient of doping concentrations to manipulate the recombination zone toward the center of the EML [90].

The selection of host materials is clearly important from a charge transport perspective, but, several other parameters also need to be considered. The key parameters in host selection include appropriate triplet energy to avoid exciton quenching, appropriate HOMO and LUMO levels to aid in charge transport and avoid exciplex formation [91, 92], high charge mobility, compatibility with the deposition process (e.g., appropriate sublimation temperature for vapor deposition techniques), high glass transition temperature (Tg) [93, 94], good electrochemical and exciton stability [95], and good morphological properties. The ideal host or host mixture should be capable of efficiently transporting both holes and electrons as well as have appropriate energy-level alignment with the adjacent blocking or charge-transporting layers. Since OLEDs are designed for emission of a wide range of spectral regions, the exact requirements of the host material will depend on the spectral demands and the particular emitter combination. Typical host materials contain many of the same moieties as electron and hole transporting moieties but the particular composition will depend on the application. Of note are host materials which contain both electron-transporting and hole-transporting moieties, often called ambipolar hosts, which provide good charge transport for both holes and elections to avoid charge build up at the EML edges. Similarly, using a blend of electron and hole transporting organic molecules in a host mixture, sometimes called exciplex hosts [96], gives the additional freedom to fine-tune the ratio of the electron- and hole-transporting components to achieve charge balance. Due to the wide variety of applications and materials for hosts, the reader should refer to a more comprehensive review [97].

Exciton Formation in Emissive Layers

When the anions and cations (electrons and holes) are brought together in the EML to nearby neighboring molecules, they can recombine to form an exciton on one of the molecules through an electron transfer leaving a ground state on the other

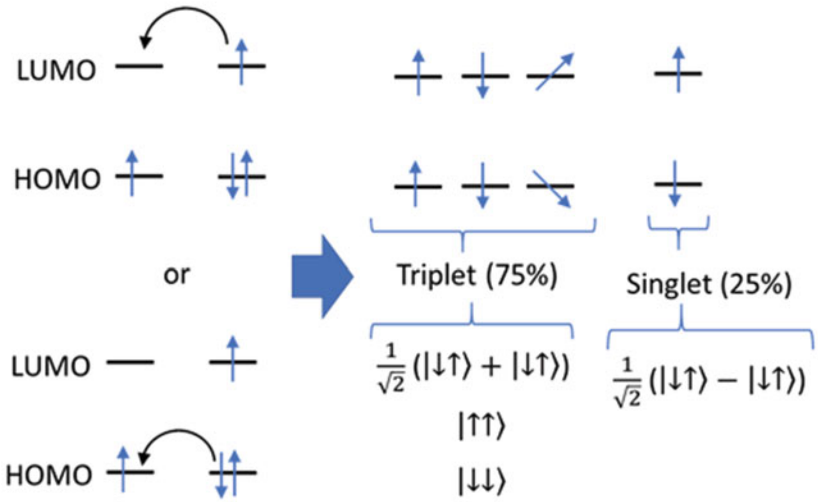

Fig. 5 Spin states in OLEDs

molecule. This can occur through either an electron transfer from the LUMO of the anion to the LUMO of cation or through the transfer of an electron on the HOMO of the anion to the HOMO of the cation. It is also possible to have an electron transfer from the LUMO of the anion to the HOMO of the cation, but this process is unfavorable due to a large amount of energy needing to be dissipated for such a transfer to occur [98]. This electron transfer results in one molecule returning to its ground state configuration and the other molecule forms an exciton. If this excited state forms between two molecules of offset energy levels an exciplex may form where the excited state is shared between the two molecules [20]. For most PHOLED applications, it is desired to form the exciton on a single emitter molecule. This process of bringing charges together to create excited states generates a statistical mixture of four different electron spin configurations (shown in Fig. 5) with 25% having a net spin of S = 0 (called a singlet) and 75% having a net spin of S = 1 (called a triplet) [8]. Most materials have a singlet ground state since they have all their electrons paired with opposite spin. Since emission of a photon typically requires spin to be conserved, 25% of the excitons created can emit while relaxing from their excited singlet state to the singlet ground state in a process called fluorescence. Decay from the other 75% of the excitons in the triplet ($S = 1$) excited state is typically a non-radiative process for most organic materials and these excitons are lost as heat. This spin conservation process is the major reason fluorescent OLEDs have limited efficiency. Phosphorescent materials on the other hand incorporate heavy metals which enable them, through strong spin–orbit coupling effects, to undergo a spin–flip process to go between singlet and triplet states [9]. Spin–orbit coupling is a quantum mechanical effect that facilitates the mixing of singlet and triplet character to

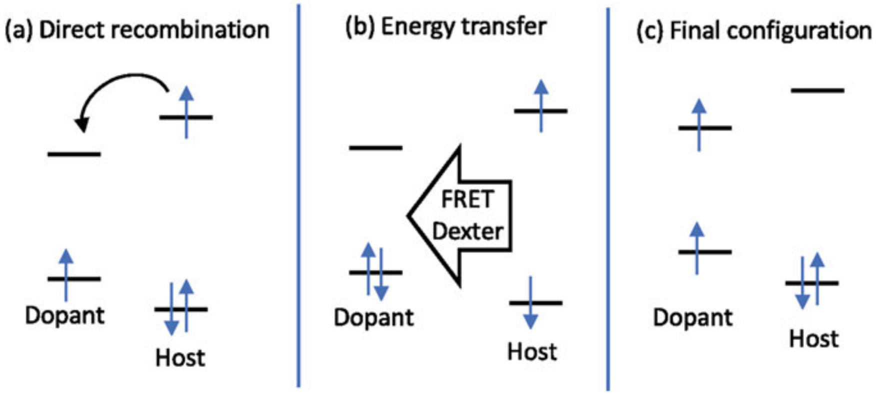

Fig. 6 Exciton formation process

allow conversion between singlet and triplet states. The strength of this interaction is proportional to the atomic number to the fourth power, so it is much more significant for heavy metals [118]. As a consequence of the strong spin–orbit coupling for heavy metal complexes, all the generated excitons formed on the phosphors are rapidly interconverted to triplets due to favorable intersystem crossing. Ultimately, the heavy metal complexes are capable of emitting from these triplet states allowing the excitons to decay radiatively in a process called phosphorescence [9, 99].

Two different mechanisms have been suggested for how excited states can be formed in doped PHOLEDs. As shown in Fig. 6a, charges can be trapped on the dopant molecule and the opposite charge can be transported to this emitter to form the exciton directly on the emitter. This has the advantage of controlling the excited state localization to only those sites where the emission process is preferred to originate. In the second case, Fig. 6b, excitons are formed on the host molecules and the excited state is then energy transferred to the emitter. Singlet excitons can be transferred over several nanometers via a non-radiative dipole coupling called Förster resonance energy transfer (FRET), while triplet excitons must energy transfer by triplet diffusion, hopping molecule by molecule, via a short-range electron exchange mechanism called Dexter energy transfer (Dexter). These two processes can be effective in transferring the energy to the emitter to form an exciton (Fig. 6c) as long as there is sufficient energetic driving force for these energy transfers to occur and high enough doping concentration of the phosphor.

Exciton Decay

Once the triplet exciton has been formed on the phosphorescent material, the energy can be transferred to another material, the excited state can relax to the ground state non-radiatively, or, preferably, the excited state can relax radiatively with the emission of a photon. This competition of radiative and non-radiative pathways is a competition of rates. Therefore, important emitter design parameters to consider are PLQY and the emission transient (τ) where ideally the PLQY will be as close to unity as possible and the transient will be as fast as possible as well as tuning the triplet energy to the desired emission color. The competition between the preferred radiative decay from the triplet state of the phosphor and the non-radiative relaxation of the excited state will be discussed in more detail in the following section. Several intermolecular pathways for the exciton to return to the ground state also exist including annihilation events with other excited or charged molecules, energy transfer to another molecule, or charge transfer quenching [81, 100]. One solution to these intermolecular interactions is to add bulky substituents which prevent aggregation or quenching effects, however, these groups can also slow charge transport leading to an increased device operating voltage and lower power efficiency [101, 102].

2.2.6 Light Extraction

Control over the charge injection and transport processes and appropriate selection of a highly efficient phosphor can lead to internal quantum efficiencies which approach 100% [11]. However, these photons created within the device still need to outcouple from the device. The ratio of the photons created to photons emitted is called the outcoupling efficiency (η_{Out}). Photons can be lost through self-absorption of the organic layers, waveguiding within the device, surface plasmon modes, and absorption of the photons in the cathode. For bottom-emitting PHOLEDs on glass substrates this results in a typical outcoupling efficiency $\eta_{\mathrm{Out}} = 20\text{–}40\%$ [26] with most of the remaining light waveguided in the substrate and the organic layers. The exact outcoupling efficiency requires a sophisticated analysis to account for the coupling of excited states to the device cavity modes [103].

Most of the methods to overcome the outcoupling limitations have focused on expanding the escape cone from the substrate and suppressing the waveguide modes in the organic layers. For example, using rough or textured surfaces [104], mesa structures [105, 106], lenses [107, 108], the use of reflecting surfaces or distributed Bragg reflectors [109, 110], incorporating a film of a scattering medium [111], or even a thin layer of a very low refractive index silica aerogel ($n_{\mathrm{i}} \sim 1.03$) in the device [112]. One of the most promising methods of enhancing the outcoupling efficiency has been the use of an ordered array of microlenses [113]. Despite the enhanced EQE using these outcoupling methods, the higher efficiency is often accompanied by changes in the angular distribution profile of the emission or changes in the emission spectrum with viewing angle. In the case of patterned displays, the blurring of the emitted light between neighboring pixels can significantly distort the image. Nevertheless, these strategies can be highly useful for lighting where pixel definition is less of a concern and the commercialization of lighting technology is driven largely by efficiency performance.

The loss of light to waveguiding in the organic layers and substrate is only a portion of the loss pathway. A substantial amount of light is also lost to surface plasmon modes. Surface plasmon polaritons (SPP) arise from oscillations of free charges at the cathode–organic interface resulting in an electric field that penetrates into the organic layers of the OLED. The excited states of phosphorescent dopants can also be considered as oscillations in electron density called “transition dipoles.” The excited state can energy transfer into the SPP modes non-radiatively, leading to a loss in emission efficiency [103]. Increasing the ETL thickness can reduce this effect but often leads to increasing losses from waveguiding effects. An elegant solution to reducing this problem is to design emitting molecules that are aligned in the thin film such that their transition dipole moment is poorly aligned for coupling to the SPP modes and can emit efficiently without interacting with this electric field. The molecular design criteria for this strategy focus on both electronic and geometric molecular modifications which can change both the direction of the transition dipole moment and influence the orientation of the molecule within the thin film [114].

3 Properties of Phosphorescent Materials

As laid out in Sect. 2, the various layers of an OLED stack can be optimized to reduce the voltage, optimize charge balance, and ensure efficient recombination but ultimately, much of the device performance hinges on the appropriate design of the phosphorescent emitter. The exact design criteria for a phosphor will depend on the specific application, but the important parameters for all phosphor designs focus on color, efficiency, emission transient, electrochemical properties, and stability.

Color: One of the most important design parameters is the emission color from the device. For pixelated active matrix displays, this means the design of red, green, and blue monochromatic pixels, whereas for lighting, it is generating devices with broad emission spectrum and uniform emission across the visible spectrum. In a phosphor, the emission color is determined primarily by the energy and molecular orbital parentage of the lowest excited triplet state. Several standards have been established to help quantify and codify the color emitted from the device. From a photophysical standpoint, some common parameters used to describe the emission of the phosphor include emission onset, the peak wavelength emission (λ_{max}), and the full width at half maximum (FWHM). Due to the simplicity and conciseness of metrics like these, research scientists will often use these parameters to compare properties of materials such as triplet energies or the character of the excited state.

The information provided by simple single wavelength metrics is an incomplete representation of the whole emission spectrum and has no consideration for the human perception of the light, both of which are crucial for both display and lighting applications. One of the most common metrics that address these issues have been developed by the Commission Internationale de l’Eclairage which developed a coordinate system and a color space in which perceived color is measured [115]. The metric, which takes into account the entire emission spectrum, uses a set of coordinates (CIEx, CIEy) on a two-dimensional XY plot of all the perceived colors which can be created. This type of standard representation of emission color affords the ability of manufacturing companies or government standard agencies to develop color standards for various technologies. Refinements to the 1931 color standard have been made over the years, for example, the 1976 standard renders a more uniform representation of color. However, the 1931 standard is still the most widely used tool in the display industry.

For lighting, additional standards are required since the perception of white lighting is not only the emission from the source (which can be represented by CIE coordinates) but also by the fidelity with which a lighting source reproduces the colors of illuminated objects. The color rendering index (CRI) is the most common scale used to evaluate the ability of white light sources to reproduce the colors of objects in comparison with an ideal or natural light source. The formal standards for CRI are also controlled by the Commission Internationale de l'Eclairage (where the value is called CIE R_a) and have a scale from 0 to 100 where 100 is a spectrum identical to daylight or any other blackbody radiation source. Another parameter for lighting, often used in lieu of CIE coordinates to describe the color of the emitted light is the correlated color temperature (CCT) which is the temperature of a black body radiation source whose perceived color is the closest to that of the white light source under study.

Efficiency: the efficiency of a phosphorescent emitter can be well described by the PLQY which is the ratio of emitted photons to absorbed photons. This metric is based on measurement with optical excitation. However, since the decay from the excited state is roughly the same for an electrically excited molecule, the PLQY is assumed to be a good representation of the efficiency of an EL device. However, since charge-exciton interactions can be deleterious to the efficiency and the exciton densities in an electrically driven device are typically much higher than optically excited films, the PLQY is typically considered the upper bound of η_{int}. Another major difference between optical and electrical excitation is the exciton formation process where optical excitation could provide a different distribution of excited states among the EML components compared to the excited states formed by direct charge trapping, for example, there could be incomplete energy transfer in optically excited PLQY measurements. Also, the PLQY in dilute solutions or inert polymer matrices could also have very different efficiencies than the PLQY of the EML composition.

Emission transient: the emission transient (τ), or excited state lifetime, is a term used to describe the decay time of the excited state on the phosphorescent material. The value for the τ is the time for a population of excited states to decay to 1/e of the initial population. Phosphorescent materials can have τ as low as 1 μs while maintaining high PLQY [133]. It is important to mention here that emission transients are typically inclusive of both non-radiative and radiative decays and are often fast for emitters with high non-radiative decay rates, so it is a good practice to consider PLQY and emission transient together. The emission transients are of crucial importance to both the device efficiency and the device operational lifetime. Since longer τ gives more time for the emitter to decompose, energy transfer, or decay non-radiatively, it is typically desired to reduce the transient to be as low as possible. This is particularly important at high drive currents where the density of excitons and charges can be high resulting in undesirable bimolecular interactions.

Electrochemical properties: In order to evaluate the charge and exciton dynamics of phosphors in devices, it is important to discuss their energy levels and the relationship of these levels to other molecules in the device. While each molecule has many energy levels, it is often appropriate to simplify the description to just frontier molecular orbitals, the HOMO and LUMO, since these are the most active orbitals for electron transfer processes. These HOMO and LUMO energies can be measured directly in the thin film from methods such as UV photoelectron spectroscopy (UPS) to determine the HOMO level or inverse photoelectron spectroscopy (IPES) to determine the LUMO energies [116]. Alternatively, due to the molecular and chemical nature of these materials, it is often convenient to estimate the HOMO and LUMO indirectly from electrochemical measurements such as cyclic voltammetry or differential pulse voltammetry [57, 117]. These electrochemical measurements can give a precise description of the oxidation and reduction processes occurring on these materials but ignore the effects of interfaces and solid-state effects. Furthermore, the cyclic voltammetry measurements can give some information on the reversibility of the redox reactions which can give insights into electrochemical stability of phosphors.

Phosphor stability: There are several methods to probe phosphor stability including chemical stability, electrochemical stability, photostability, etc., each of which can provide some information about the phosphor but ultimately the degradation in a device which contains high local electric fields, large concentrations of charges, and excited states is a complicated system to emulate outside a device. Therefore, the ultimate test of the stability of a phosphor is to carry out operational life testing on test pixels using the phosphorescent emitter. This typically involves fabricating a small pixel or series of pixels and driving them at a constant current density while measuring the luminance loss over time. The metrics used to report operational lifetime are therefore the time to decay to a given percent of initial luminance at a specific driving condition. The percentage luminance loss and device driving conditions used to quantify device lifetime vary wildly in the literature with everything from LT97 (decay to 97% of initial luminance) to LT50 or half-life (decay to 50% of initial luminance) and driving conditions of 1 mA/cm^2 to 10 s of mA/cm^2 or even initiating the driving condition at the current which has an initial luminance of 1000 cd/m^2. All of these metrics can make comparing device operational lifetimes between reports challenging and often the use of stretched exponential fits or application of acceleration factors is required to interpolate or extrapolate lifetime curves to a comparable metric.

3.1 Photophysical Processes in Phosphorescent Materials

One of the key steps in the generation of electroluminescence is the exciton decay process, the step in which a photon may be created from a molecule in its excited state returning to the ground state. Since this process typically concerns neutral molecules in their excited and ground states, it is analogous to the decay processes in photoluminescence and it is easy to visualize with a Jablonski diagram shown in

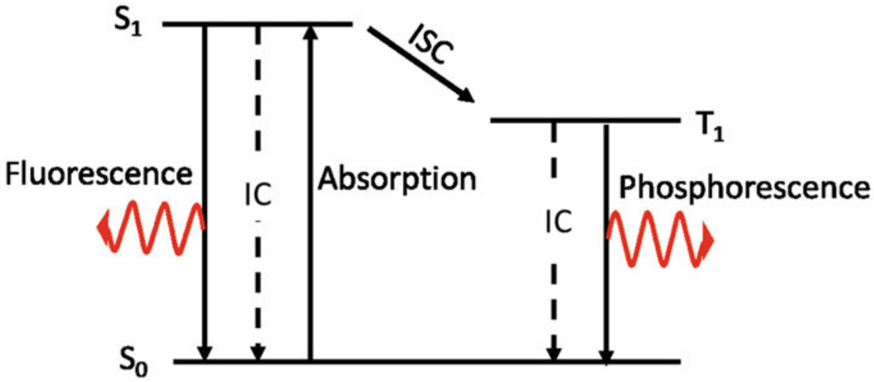

Fig. 7 Jablonski diagram

Fig. 7 [118]. This type of diagram is a simplified schematic representation of the various states of interest and processes of interchanging between them. In a more accurate representation, each state would be a complex potential energy surface all of which contain a large number of vibrational levels.

To a first approximation, the photophysical processes of many molecules can be described by a three-state system: the ground state (S_0), lowest singlet excited state (S_1), and the lowest triplet excited state (T_1). In photoluminescence, the excited states are accessed initially by the absorption of a photon (represented by the solid line $S_0 \rightarrow S_1$) show in Fig. 7. In an EL process, the population of the S_1 will occur by either energy transfer or direct charge recombination as was discussed in Sect. 2.2.4 rather than by the absorption of a photon. The population of higher lying excited states in either photoexcitation or electrical excitation typically thermalize to the lowest excited states S_1. Following the population of the S_1 state, the molecule can take several pathways to relax back to the ground state. The excited singlet can radiatively relax to the ground state emitting a photon by fluorescence (represented by the solid line $S_1 \rightarrow S_0$). This process can occur quickly, on the order of nanoseconds [118], and many types of fluorescent materials can primarily relax through this process with high PLQY. In some cases, other deactivation pathways are competitive with fluorescence. Non-radiative decay from the S_1 (represented by the dashed line $S_1 \rightarrow S_0$) is a broad term to describe various thermal deactivation processes, called internal conversion (IC) in which the excited states thermalize through accessing various molecular vibrations to the ground state [118]. One pathway of particular importance to PHOLEDs is the intersystem crossing (ISC) from $S_1 \rightarrow T_1$. In an EL device, the recombination of charges can also form an excited state in the T_1 directly. Relaxation from this excited state can also occur via emission of a photon through phosphorescence (represented by the solid line $T_1 \rightarrow S_0$), or by thermal non-radiative deactivation (represented by the dashed line $T_1 \rightarrow S_0$). In organic materials, the direct relation from $T_1 \rightarrow S_0$ is symmetry forbidden and consequently very slow with luminescent lifetimes in the range of seconds. Organometallic complexes containing