Review of recent progress in multilayer solution-processed organic light-emitting diodes

Szuheng Ho
Shuyi Liu
Ying Chen
Franky So

Review of recent progress in multilayer solution-processed organic light-emitting diodes

Szuheng Ho, Shuyi Liu, Ying Chen, and Franky So*

University of Florida, Department of Materials Science and Engineering, 100 Rhines Hall, P.O. Box 116400, Gainesville, Florida 32611-6400, United States

Abstract. Organic light-emitting diodes (OLEDs) have become a promising candidate for lighting and display applications. High efficiency OLEDs require a multilayer device architecture to provide exciton confinement and balance charge transport. Conventional OLEDs are made by vacuum process, and the manufacturing cost can be reduced by solution processing. However, unlike vacuum-deposited OLEDs, solution-processed multilayer OLEDs are more challenging to make. The key for multilayer solution processing is to have the layer structure which can withstand solvents used in subsequent processing. We review the materials' strategies to make multilayer solution-processed OLEDs. Specifically, we will discuss the use of cross-linkable organic materials, metal oxides, and orthogonal solvent systems to deposit various functional layers in an OLED. © *2015 Society of Photo-Optical Instrumentation Engineers (SPIE)* [DOI: 10.1117/1 .JPE.5.057611]

1 Introduction

The first organic light-emitting diode (OLED) was demonstrated by Tang and VanSlyke[1] and the device was a small-molecule organic bilayer device sandwiched between two electrodes. At the end of the 1990s, since the invention of phosphorescent emitters by Baldo et al.[2] and Adachi et al.,[3] the structure of an OLED has become more complicated, with multiple functional layers acting as charge injection, charge transport, exciton blocking, and emitting layers (EMLs).

Multilayer devices can be made by vacuum deposition, and commercial OLEDs are currently made with this process.[4–11] However, vacuum thermal evaporation bears the drawbacks of low material utilization rates, poor scalability, high capital cost, and difficulty in patterning. Solution processing, in principle, provides a low-cost approach to fabricate OLEDs. Early solution-processed OLEDs were based on a simple architecture with an emitting polymer layer and a hole injection polymer layer.[12–15] Recently, more attempts have been made on solution-processed small-molecule OLEDs with mixed EML.[16–20] However, without using a multilayer architecture, the performance of solution-processed OLEDs is inferior to evaporated OLEDs.

To fabricate solution-processed multilayer OLEDs, intermixing of layers is a major issue because the deposition of a layer may dissolve or intermix with the preceding layer. Tremendous efforts have been made to circumvent this issue. One approach is to use orthogonal solvent systems, where the difference of material solubility in different solvents is employed to process adjacent layers without intermixing. An example is the widely used water soluble poly (3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) hole injection layer (HIL) with a subsequent hole transport layer (HTL), which is usually soluble in organic solvents. The second approach is to use photo or thermal cross-linkable organic functional materials for OLEDs. Because the cross-linked functional layer is not soluble in solvents, subsequent

---

*Address all correspondence to: Franky So, E-mail: fso@mse.ufl.edu

deposition of another layer should not interfere with the underlying layer. The third approach is to introduce inorganic functional materials such as metal oxides into OLEDs. Again, these metal oxides are not soluble in organic solvents which enable processing of subsequent layers.

In this review, we describe these materials for solution-processed OLEDs. The objective of this review is to describe these approaches to address the problems associated with multilayer device processing, especially for HIL/HTL, EML, and ETL. In addition, an overview of solution-processed multilayer device applications will be presented, followed by the future prospects and direction for solution-processed multilayer OLEDs.

2 Hole Injection/Transport Layers

2.1 Hole Injection Materials

2.1.1 Hole injection polymers

Most polymer-based HILs/HTLs are aqueous-based and insoluble in organic solvents, which make them suitable for orthogonal solvent processing. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate, known as PEDOT:PSS, has been widely used as an HIL in organic electronic devices in the past.[21] Currently, the PEDOT:PSS HIL for organic optoelectronic devices is commercially available from Heraeus Holding GmbH under the brand of Clevios™.[22,23] The use of PEDOT:PSS in solution-processed multilayer OLEDs have been previously reviewed by Zhong et al.[24] and readers are referred to this work for the early development and application. The easy processing by spin casting from aqueous solution makes PEDOT:PSS a popular HIL/HTL. PEDOT:PSS bears the merits of high conductivity and high transparency along with its good film forming property and its ability to planarize the indium tin oxide (ITO) surface. However, there are device stability issues associated with PEDOT:PSS as an HIL. First, PEDOT:PSS has a high acidity (with pH value ranging from 1.0 to 2.5), and corrodes the ITO electrode, leading to device degradation. Second, PEDOT:PSS absorbs moisture, which is another source of device degradation. Third, its work function is -5.2 eV and the hole injection barrier from HIL into HTL or EML leads to the accumulation of carriers at the HTL interface, resulting in device degradation. Extensive research has been done on modifying or identifying alternatives for PEDOT:PSS as a hole injection material.

Lee et al. introduced perfluorinated ionomer (PFI) dopant to modify PEDOT:PSS to a self-organized gradient hole injection layer (GradHIL).[25–32] The driving force for self-organizing behavior is from the more hydrophobic nature of the fluorocarbon chains in PFI, making it preferentially stay at the surface of the film. By tuning the ratio of PEDOT/PSS/PFI, the work function (ϕ) can be tuned from 5.05 to 5.70 eV as the content of PFI increases,[25] which enables its value to match the highest occupied molecular orbital level of the EML. Since PFI with fluorocarbon chains is more hydrophobic than the polystyrene chain, PFI tends to reside away from ITO and form a "self-organized" gradient, rendering a work function gradient in the HIL. In addition to reducing the injection barrier, the PFI-doped PEDOT:PSS can inhibit diffusion of indium and tin. Time-of-flight secondary ion mass spectroscopy data reveal that the fluorinated surface from PFI can retard the out-diffusion of In or Sn from the ITO anode, which is important to improve the device lifetime. The half lifetime from 1000 cd/m^2 in solution-processed green polymer LED is 2680 h with GradHIL, compared to that of 52 h without PFI modification.[26] Han et al.[28] integrated the GradHIL with graphene and successfully achieved the power efficiency of 85 lm/W in phosphorescent OLEDs (PhOLEDs) and 24 lm/W in fluorescent OLEDs.

In addition to modifying PEDOT:PSS, polyaniline (PANI) and its blends serve as alternative HILs. PANI is by nature insoluble in common solvents.[33,34] The solution processable PANI is a blend protonated by functionalized protonic acids such as camphorsulfonic acid[35] or copolymers of aniline and sulfonated aniline derivatives (PANI:PSS).[36] Jang et al.[34] demonstrated that PANI:PSS has a higher transmittance and a smoother surface than PEDOT:PSS for contacts with subsequent organic layers. Fehse et al. fabricated multilayer OLEDs using D1033 PANI dispersion with efficient carrier injection and high power efficiencies.[37] Choi et al.[27,38] also incorporated PFI into PANI:PSS to increase its work function similar to that in PEDOT:PSS. With an optimal ratio

of PANI:PSS:PFI, a fluorescent OLED using Bis(10-hydroxybenzo[h] quinolinato)beryllium ($Bebq_2$) as an emitter shows a maximum current efficiency of 19 cd/A.

More recently, Choudhury et al.[39] and Chen et al.[40] demonstrated polythienothiophene doped with poly(perfluoroethylene-perfluoroethersulfonic acid) (PTT:PFFSA) with enhanced hole injection efficiency. Its work function is tunable from 5.2 to 5.7 eV, which serves as a buffer step between ITO anode and HTL. From the dark injection-space charge limited current (DI-SCL) measurement, the hole injection efficiency of PTT:PFFSA is 1.5 times that of PEDOT:PSS, resulting in a device lifetime enhancement compared with devices using PEDOT:PSS. The reasons for improved lifetime is attributed to the deeper lying work function of PTT:PFFSA such that fewer charges are trapped between the HIL and HTL interface, suppressing degradation from the exciton quenching centers. Since HIL plays a crucial role in device degradation, a stable HIL is desirable for state-of-the-art OLEDs.

Orselli et al.[41] and Ho et al.[42] along with Plextronics Incorporation reported stable aqueous or nonaqueous HILs for PhOLEDs. Plexcore® OC AQ1200 (AQ1200) has a reduced acidity (with a pH value from 2.6 to 3.4) with a better air stability, as shown in Fig. 1. When OLEDs are fabricated with AQ1200 HIL, the degradation due to moisture uptake and acidity of HIL can be minimized. With a work function ranging from 5.3 to 5.7 eV, the hole injection barrier is reduced. Green PhOLEDs with AQ1200 show a maximum current efficiency of 68 cd/A at a luminance of 200 cd/m^2 and the half lifetime (LT50) at 1000 cd/m^2 is 8400 h.

The resistivity and the work function of the aforementioned polymer-based HILs—including PEDOT:PSS:PFI, PANI:PSS(:PFI), and AQ1200—are tunable, and they have the potential to substitute for ITO as conducting polymer electrodes on flexible substrates. The properties of these HILs are summarized in Table 1. These HILs have low solubility in common organic solvents, which makes them resistive to solvent rinse during processing and suitable for multilayer solution process fabrication.

2.1.2 Small molecule

1,4,5,8,9,11-Hexaazatriphenylene hexacarbonitrile (HAT-CN), an evaporated HIL material which has been widely used in OLEDs, is also reported for fabricating multilayer solution-processed OLEDs. Lin et al.[43] recently adapted the compound for solution processing using 2-propanone as a solvent. Red, green, and blue OLEDs fabricated with HAT-CN HIL showed
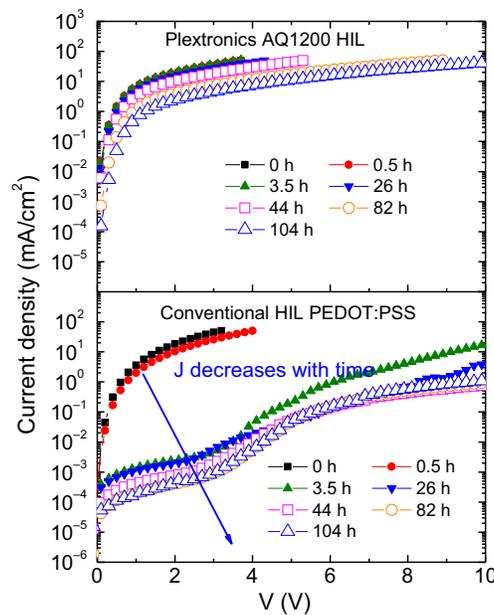

Fig. 1 The current density–voltage ($J – V$) characteristic variation with time for devices with AQ1200 and PEDOT:PSS under ambient condition. Reprinted with permission from Ref. 42. Copyright (2014), Elsevier.

Table 1 Properties of various polymer-based hole injection layer (HIL) materials.

Material	ϕ (eV)[a]	σ (S/cm)	pH	Note	Reference
Baytron/Clevios PEDOT:PSS					
PVP AI 4083[b]	5.0 to 5.2	2 to 20 × 10^{-4}	1.2 to 2.2		22 and 23
P CH 8000[b]	—	3 to 10 × 10^{-4}	1.0 to 2.0		22 and 23
PH 500[b]	4.8 to 5.0	500	1.5 to 2.5		22 and 23
PH 1000[b]	4.8 to 5.0	1000	1.5 to 2.5		22 and 23
PEDOT:PSS:PFI	5.3 to 5.7	—	—	Property dependent on doping ratio	25
Plextronics/Plexcore OC					
AQ-1200[c]	5.3 to 5.7	3 to 20 × 10^{-4}	2.6 to 3.4		42
RG-1100[c]	5.1 to 5.2	4 to 40 × 10^{-4}	2.2 to 2.8		41
PTT:PFFSA	5.2 to 5.5	—	2.2 to 3.5		39
PANI:PSS	5.2	—	—		27
PANI:PSS:PFI (GradHIL)	5.8 to 6.0	—	—	Property dependent on doping ratio	27
PSS-g-PANI:PFI	5.8 to 6.1	—	—	Property dependent on doping ratio	38

[a]Values measured by ultraviolet photoelectron spectroscopy.
[b]Trade name of Heraeus Holding GmbH.
[c]Trade name of Plextronics Incorporation.

high power efficiencies of 15, 55, 16 lm/W, respectively. Because of the enhanced efficiency and stability, small-molecule HILs are widely used in OLED manufacturing today.

2.2 Cross-Linkable Materials for HTLs

In most OLEDs, there is a large barrier for hole injection from a typical HIL (PEDOT:PSS) into the EML, thereby limiting the device performance. In vacuum-deposited OLEDs, this limitation has been overcome by inserting an HTL between HIL and EML, providing an intermediate step for hole injection. For solution-processed devices, the dissolution of the preceding layer by the solvent of the subsequent layer makes multilayer processing a difficult task. One solution is to chemically cross-link the functional layer such that layer-by-layer stacking is feasible without intermixing between the adjacent layers. The prevailing cross-linking chemistry is to attach functional cross-linkers to the functional molecules.[44,45] In this section, we review conventional HTLs modified with the following cross-linking groups: oxetanes, styrenes, trifluorovinyl ethers, and benzocyclobutene (BCB).

2.2.1 Oxetane-based HTLs

Under ultraviolet (UV) illumination, oxetane-based HTLs can initiate cross-linking via cationic ring-opening polymerization (CROP) and form linear polyethers.[46,47] Yang et al.[13] have reported a series of cross-linkable HTLs (X-HTLs) based on adding sidechains containing four-membered cyclic ethers to conventional HTLs. Cross-linkable N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) derivatives (N,N'-bis(4-(6-((3-ethyloxetan-3-y)methoxy)-hexyloxy)penyl-N,N'-bis(4-methoxyphenyl)biphenyl-4,4'-diamin (QUPD) and N,N'-bis(4–(6–((3–ethyloxetan-3-y)methoxy))-hexylpenyl)-N,N'-diphenyl-4,4'-diamin (OTPD), as shown in Fig. 2, were synthesized and used in OLEDs by multilayer solution process. By using a
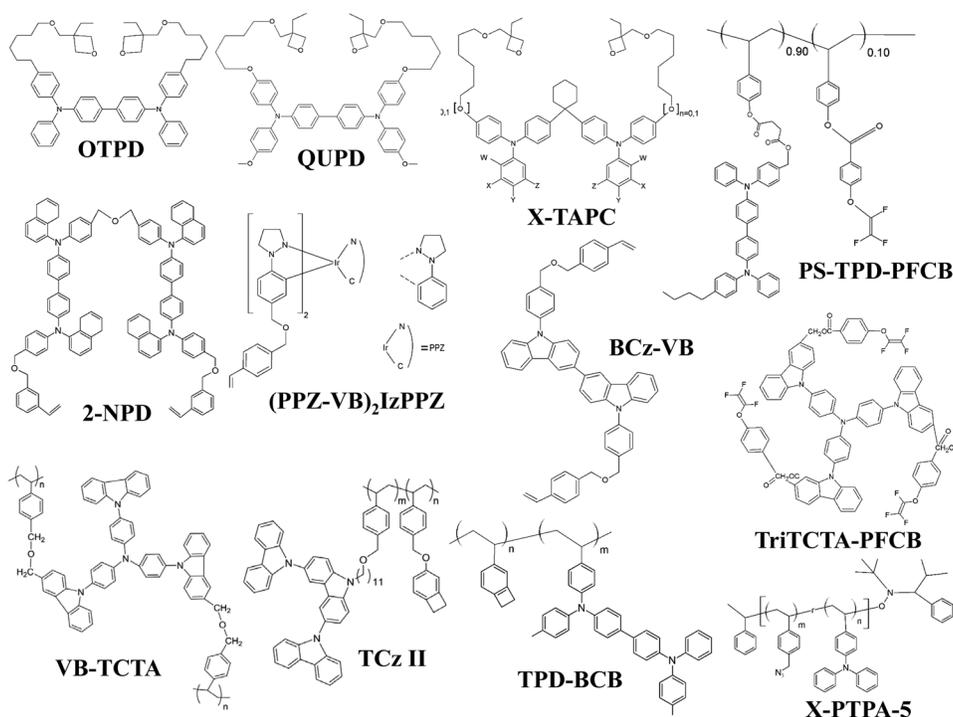
Fig. 2 Cross-linkable hole transport layers.

combination of two cross-linkable HTLs, the barrier height can be divided into two smaller steps. The current efficiency showed a threefold enhancement from ∼20 to 67 cd/A.[13,48,49] External quantum efficiencies (EQE) of 11%, 19%, and 6% were achieved in red, green, and blue OLEDs, respectively. A further electromodulation study suggests the effect of X-HTLs not only creates facile hole injection but also confines electrons at the EML/HTL interface, resulting in an efficiency enhancement.[50,51] Another series of oxetane functionalized X-HTLs with high triplet energies and large bandgap energies were synthesized based on 1-bis[4-[N,N′-di(4-tolyl)amino]phenyl]-cyclohexane, resulting in an improved efficiency (18 cd/A), and a reduced efficiency roll-off was observed in blue devices.[52,53] Generally, this type of cross-linking reaction occurs at lower temperatures with a rapid reaction rate. However, owing to the use of photoacids, it is inevitable to have residual side products or initiators in the cross-linked X-HTLs which might impair the device stability. To initiate the cross-linking reaction via a photoacid-free path, Köhnen et al.[46] proposed a concept of layer by layer cross-linking. The cross-linking reaction is activated by protons from the excess PSS of the acid PEDOT:PSS layer. The reaction then moves away from the PEDOT:PSS interface and throughout the X-HTL. Additionally, introducing a postannealing after UV illumination can alleviate this issue.[44]

2.2.2 Styrene-based HTLs

In addition to photo cross-linking, thermal cross-linking is another option. In this case, neither photoacid nor initiator is required, thus eliminating one of the factors giving rise to exciton quenching and stability problems. To form polymer networks, generally, two styryl [or termed vinyl benzyl (VB)] groups are functionalized to the HTL molecules. The typical curing temperature is higher than 150°C, requiring the hole transport moiety to be sustainable to the high curing temperature. Liu et al.[54] and Niu et al.[55] reported a cross-linkable 4,4′,4″-tris-(N-carbazolyl)-triphenlyamine (TCTA) derivatives (VB-TCTA) as an HTL. White OLEDs with VB-TCTA as HTL have a current efficiency of 11 cd/A (EQE of 6%). Another conventionally evaporated HTL, N,N′-bis(1-naphthyl)-N,N′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPD), was also reported with styrene functionalized derivatives (1-NPD, 2-NPD) for the cross-linking reaction. These HTLs can be cured at 230°C for 30 min, and a green polymer LED (PLED) with PEDOT:PSS/2-NPD (HIL/HTL) exhibits a current efficiency of 11 cd/A.[56] Ma et al.[57]

incorporated VB ether to iridium-based 1-phenylpyrazole, (PPZ-VB)$_2$IrPPZ. Green OLEDs with this X-HTL show a power efficiency of 14 lm/W (EQE of 8.5%). Recently, Jiang et al.[58] reported a high efficiency small-molecule OLED with X-HTL based on 3,3′-bicarbazole (BCz) with two VB ether units (BCz-VB). BCz-VB has a high triplet energy and relatively lower curing temperature of 146°C and the resulting blue OLEDs [iridium(III) bis[(4,6-difluorophenyl)-pyridinato-N,C2]picolinate, FIrpic] show a current efficiency of 25 cd/A and a turn-on voltage of 5.6 V, which makes styrene-functionalized HTLs promising X-HTLs.

The ratio of the insulating cross-linkable moiety to the transporting one is critical to UV/thermal curing process and also the device efficiency.[59] It is anticipated that the solution-processed X-HTL can perform comparable to its evaporated counterparts. Xiang et al.[60] demonstrated a styrene functionalized NPD derivative in phosphorescent orange OLEDs. With optimized orange EML and cesium carbonate (Cs$_2$CO$_3$)-doped electron transport layer (ETL), the OLED efficiency and stability from this X-HTL are comparable to those from vacuum-deposited 4,4′-bis[N-(1-naphthyl)-N-phenylamino]biphenyl device.

2.2.3 *Perfluorocyclobutane-based and BCB-based HTLs*

Perfluorocyclobutane (PFCB)-based cross-linkable groups have been used for X-HTLs. Niu et al.[61] used PFCB functionalized TPD on polystyrene backbone (PS-TPD-PFCB) and PFCB-modified TCTA (TriTCTA-PFCB) in blue OLEDs with a very low EQE of 1%. On the other hand, a BCB group can also undergo thermal dimerization. Ma et al.[62] introduced the BCB-modified TPD derivative (TPD-BCB) and the PhOLEDs with TPD-BCB as HTL exhibited a maximum EQE of 10%. However, the cross-linking reaction requires 180°C for 2 h, followed by another 4 h baking at 250°C, which is challenging for processing. Zuniga et al. reported a method to cross-link the HTL by rapid thermal annealing (RTA) to prevent PFCB/BCB-based X-HTLs from being exposed to high temperatures for long time.[63] A curing condition with a higher temperature but much shorter curing time was applied to 3,6-bis(carbazol-9-yl)carbazole with BCB moiety (TCz II). The green PhOLEDs fabricated by the RTA process have a high efficiency (48 cd/A) compared to the ones processed by conventional long-time annealing on a hotplate (27 cd/A).

2.2.4 *Other cross-linking chemistries*

There are other functional groups that can undergo polymerization, dimerization, or condensation to create a robust layer impervious to solvents of the subsequent layer. For example, siloxane derivatives can proceed cross-linking with the presence of moisture[64,65] and azide-based X-HTLs cross-link under UV irradiation. The triphenylamine derivative (X-PTPA-5) bears the advantage of a short UV exposure time. A current efficiency of 44 cd/A was demonstrated in green PhOLEDs.[59] Photo cross-linking also makes the micron-scaled patterning viable since the photolithography can be applied directly. Lee et al.[66] reported the thiolene reaction for photo cross-linking allyl-TFB [poly(9,9- dioctylfluorene-co-N-(4-butylphenyl)diphenylamine)], making solution-processed Ir-based green devices with a current efficiency of 31 cd/A. A summary of these cross-linkable HTLs are shown in Table 2.

The UV-initiated X-HTLs, such as oxetane-based HTLs, enables the potential for easy pixel patterning. But the reaction usually proceeds with photoinitiators which pose an adverse effect on device performance and stability. Another cross-linking chemistry is to initiate the reaction by thermal treatment. For example, the styrene-based HTLs form insoluble films under annealing temperatures at 150 to 180°C, whereas the X-HTLs with PFCB and BCB functional groups generally require a longer curing time and higher temperature. The former case seems more promising for device application because the annealing temperature is moderate for the carrier transporting moieties. The initiator-free thermal cross-linking HTLs also reduce the exciton quenching by impurities. To date, there is still a lack of systematic study on the effect of various cross-linking functional groups on material properties and device performance. Efforts on studying this issue will provide a deeper insight in the design of cross-linkable HTL materials.

Table 2 The device structure and performance of an organic light-emitting diode using X-hole transport layers (HTLs).

Material	Device structure	Efficiency	Reference
QUPD/OTPD	ITO/PEDOT:PSS/QUPD/OTPD/PVK:PBD:OXD-7:emitter/CsF/Al R: Ir(piq)$_2$(acac); G: Ir(mppy)$_3$; B: FIrpic	R: 10.8%; G: 10.8%; B: 5.7%	13
X-TAPC	ITO/PEDOT:PSS/X-TAPC/PVK:OXD-7:FIrpic/CsF/Al	18.4 cd/A	52 and 53
VB-TCTA	ITO/PEDOT:PSS/VB-TCTA/PVK:FIrpic:Ir(ppy)$_3$:Os-R1/TPBi/CsF/Al	10.9 cd/A (5.9%)	54 and 55
2-NPD	ITO/PEDOT:PSS/2-NPD/PFBT5/CsF/Al	10.8 cd/A	56
(PPZ-VB)$_2$IrPPZ	ITO/(PPZ-VB)$_2$IrPPZ/TPA-b-OXA:TPY$_2$Iracac/Cs$_2$CO$_3$/Al	14.2 lm/W (9.2%)	57
BCz-VB	ITO/PEDOT:PSS/BCz-VB/PVK:OXD-7:FIrpic/TPBi/Cs$_2$CO$_3$/Al	24.5 cd/A	58
PS-TPD-PFCB, TriTCTA-PFCB	ITO/PS-TPD-PFCB/TriTCTA-PFCB/PVK:FIr6/TPBi/CsF/Al	2.4 cd/A (1.2%)	61
TPD-BCB	ITO/TPD-BCB/TPA-OXA:TPY$_2$Iracac/BCP/LiF/Al	10.4%	62
TCz II	ITO/TCz II/P1:P2:Ir(pppy)$_3$/BCP/LiF/Al/Ag	48.4 cd/A (13.6%)	63
X-PTPA-5	ITO/PEDOT:PSS/X-PTPA-5/PVK:PBD:Ir(ppy)$_3$/LiF/Al	43.7 cd/A (11.8%)	59
Plexcore® HTL	ITO/AQ1200/Plexcore® HTL/NPB:Ir(2-phq)$_3$/BAlq/Bphen:Cs$_2$CO$_3$/Al	18.0 cd/A	60

Note: Full name of the materials: QUPD: N,N'-bis(4-(6-((3-ethyloxetan-3-y)methoxy)-hexyloxy)penyl-N, N'-bis(4-methoxyphenyl)biphenyl-4,4′-diamin; OTPD: N,N'-bis(4–(6–((3–ethyloxetan-3-y)methoxy))-hexyl-penyl)-N,N'-diphenyl-4,4′-diamin; PVK: poly(N-vinylcarbazole); PBD: 2-(4-tert-butylphenyl)-5-biphenylyl-1,3,4-oxadiazole; OXD-7: 1,3-bis[2-(4-tert -butylphenyl)-1,3,4-oxadiazo-5-yl]benzene; Ir(piq)$_2$(acac): bis (1-phenylisoquinoline)(acetylacetonate) iridium(III); Ir(mppy)$_3$: tris[2-(p-tolyl)pyridine] iridium(III); FIrpic: bis[(4,6-difluorophenyl)-pyridinato-N,C2]picolinate iridium(III); TPBi: 2,2′,2″ (1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole); PFBT5: poly[2,7-(9,9′-dihexylfluorene)-co-4,7-(2,1,3-benzothiadiazole)]; FIr6: bis(2,4-difluorophenylpyridinato)tetrakis(1-pyrazolyl) borate iridium(III); BCP: 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline; NPB: 4,4′-bis[N-(1-naphthyl)-N-phenylamino]biphenyl; Ir(2phq)$_3$: tris(2-phenylquino-line) iridium(III); BAlq: bis(2-methyl-8-quinolinolate)-4-(phenylphenolato) aluminium; Bphen: 4,7-diphenyl-1,10-phenanthroline; X-TAPC, VB-TCTA, Os-R1, 2-NPD, (PPZ – VB)$_2$IrPPZ, TPA-b-OXA, TPA-OXA, TPY$_2$Iracac, BCz-VB, PS-TPD-PFCB, TriTCTA-PFCB, TPD-BCB, TCz II, P1, P2, Ir(pppy)$_3$, X-PTPA-5, Plexcore® HTL: full names are not shown in the original papers; only the chemical structures are given in the original references.

2.3 *Metal Oxides and Inorganic Materials for Hole Injection/Transport Layers*

As an alternative to small-molecule/polymer functional layers, solution-processed metal oxides provide an inorganic option to fabricate hybrid organic–inorganic light emitting diodes (HyLEDs). The high transparency in the visible spectrum, robust film forming property, and compatibility to solution process makes metal oxides a promising candidate for carrier transporting layers in solution-processed multilayer HyLEDs. Based on their charge transport properties and energy level alignment, they are used as an HIL, HTL, ETL, and electron injection layers to fabricate a multilayer device. Compared to their organic counterparts, metal oxides have favorable characteristics for devices such as high carrier mobility, tunable energy-level alignment, and good stability. Precursors with transition metal complexes are synthesized and dissolved into polar solvents and then spin cast onto electrode substrates.[67–69] An oxidation process in ambient atmosphere is usually necessary to transform the precursors into metal oxides.

2.3.1 *N-type metal oxides for HILs*

Most transition metal oxides are n-type semiconductors. Several transition metal oxides such as tungsten oxide (WO$_3$), molybdenum oxide (MoO$_3$), and vanadium pentoxide (V$_2$O$_5$) have very

deep valence band maxima and are strong electron acceptors.[70–73] When they are in contact with ITO, there is a strong vacuum level shift resulting in the formation of an interface dipole at the ITO interface and reduction in hole injection barriers. Below is the summary of these solution-processed metal oxides for HIL applications.

MoO$_3$. Höfle et al.[74] prepared solution-processed MoO$_3$ films by spin casting a molybdenum (V) ethoxide [Mo(OEt)$_5$] ethanol solution, followed by annealing at 150°C under ambient conditions. The ionization potential (IP) and electron affinity (EA) vary slightly with respect to precursors (nanoparticle or sol-gel) and processing environments (in air or inert gas). Solution-processed MoO$_3$ generally has an IP of ~8.0 eV and an EA of ~5.0 eV. Solution-processed phosphorescent HyLEDs employing MoO$_3$ HIL showed enhanced hole injection as well as superior device performance compared to the devices with PEDOT:PSS.[74] Similarly, Jian et al.[75] synthesized MoO$_3$ with ammonium molybdate [(NH$_4$)Mo$_7$O$_{24}$ · 4H$_2$O] precursors to deposit a thick (>100 nm) HIL for large area tris(2-phenylpyridine)iridium [Ir(ppy)$_3$] devices. Due to the good transport properties of the MoO$_3$ layer, the device performance is not significantly hindered by the thickness of the MoO$_3$ films. HyLEDs with solution-processed MoO$_3$ and EML show a current efficiency of 51 cd/A.[75] Fu et al.[76] reported a room-temperature synthesis for MoO$_3$. The operational lifetime of the solution-processed green phosphorescent HyLEDs incorporating MoO$_3$ HILs was improved by two times with respect to that of the corresponding PEDOT:PSS devices.[76]

WO$_3$. The WO$_3$ HILs were fabricated from an ethanol diluted or tungsten(VI) ethoxide [W(OEt)$_6$] precursor solution at room temperatures with a ϕ of 6.7 eV.[77–79] Solution-processed blue phosphorescent HyLEDs incorporating WO$_3$ HIL showed a 75% enhancement of current efficiency compared to that of the PEDOT:PSS device.[78] Youn et al.[80] also reported a substantially improved operational lifetime of 1.8×10^6 h and a current efficiency of 10 cd/A at 1000 cd/m^2 for the super yellow devices by sandwiching PEDOT:PSS between two separate WO$_3$ layers, which effectively suppressed indium diffusion and acid damage on ITO by PEDOT:PSS.

V$_2$O$_5$. V$_2$O$_5$ precursor solutions can be prepared by vanadium pentoxide powder or vanadium (V) oxitriisopropoxide dissolved in 2-propanol.[81,82] Similar to MoO$_x$, V$_2$O$_5$ also has a deep ϕ of ~5.6 eV.[83] Kim et al.[81] and Lee et al.[83] reported a low temperature treatment for V$_2$O$_5$, which showed comparable device efficiencies and improved operational stability. Kim et al.[81] applied V$_2$O$_5$-doped PEDOT:PSS in PLED and demonstrated over 20% efficiency improvement to 15 cd/A. However, all of the above-mentioned metal oxides are n-type with a deep EA, thus lacking the appropriate energy levels to block the electrons.

2.3.2 *P-type metal oxide for HTL*

NiO$_x$. Nickel oxide (NiO$_x$) is one of the few p-type metal oxides. Its conduction band minimum is −1.7 eV, which is effective for blocking electrons in an OLED. Solution-processed NiO$_x$ has been used as an HTL in organic photovoltaics (OPV) devices.[84] Synthesis of NiO$_x$ films requires a high annealing temperature (>500°C) and UV-ozone treatment. Solution-processed NiO$_x$ has a high hole mobility of 0.14 cm^2/Vs. The hole injection efficiency measured by DI-SCL was 0.85, ~70% higher than that of PEDOT:PSS. Recently, Liu et al.[85,86] demonstrated a solution-processed green phosphorescent HyLEDs incorporating NiO$_x$HIL/HTL, with a high current efficiency of 70 cd/A and a power efficiency of 75 lm/W.

2.3.3 *Copper thiocyanate as HTLs*

Perumal et al.[87] recently reported solution-processed copper thiocyanate (CuSCN) as an HIL/HTL in green PhOLEDs. CuSCN is a p-type semiconductor and transparent across the visible spectrum. CuSCN has a valence band maximum of −5.5 eV, providing efficient hole injection into common organic HTLs. The conduction band minimum is very shallow (−1.8 eV), which is an effective electron blocker. Solution-processed OLEDs with CuSCN HTL and Ir-based EML exhibited a maximum current efficiency of 51 cd/A and power efficiency of 55 lm/W.

The development of solution-processed metal oxides HTLs has been motivated by the success of the evaporated counterparts. The precursors suitable for low temperature processing are largely

Table 3 The HyLEDs with solution-processed inorganic HIL/HTL.

Material	Device structure	Efficiency (cd/A)	Lifetime (h)	Reference
MoO$_3$	ITO/MoO$_3$/soln. TCTA:TAPC:Ir(ppy)$_3$/TPBi/LiF/Al	51.5	—	75
	ITO/MoO$_3$/soln. TCTA:Ir(ppy)$_3$/TPBi/LiF/Al	58.6	~120 [a]	76
WO$_3$	ITO/WO$_3$/soln. TCTA:FIrpic/TPBi/LiF/Al	14.0	—	78
	ITO/WO$_x$/PEDOT:PSS/WO$_x$/soln. PDY-132/LiF/Al	9.9	1.8×10^6 [b]	80
V$_2$O$_5$	ITO/V$_2$O$_5$/TAPC/evap. CBP:Ir(ppy)$_2$(acac)/TmPyPB/LiF/Al	65.0	—	83
	ITO/V$_2$O$_5$/soln. Super Yellow/LiF/Al	~7.0	>20 [c]	83
	IZO/PEDOT:PSS:V$_2$O$_5$/soln. PDY-132/LiF/Al	15.1	—	81
NiO$_x$	ITO/NiO$_x$/soln. CBP:Ir(mppy)$_3$/3TPYMB/LiF/Al	70.0	—	85
CuSCN	ITO/CuSCN/soln. TCTA:26DCzPPy:(PPy)$_2$Ir(acac)/B3PTMPM/Ca/Al	51.0	—	87

[a]Half lifetime (LT50).
[b]Projected LT50 at 1000 cd/m^2.
[c]Lifetime to 75% of initial luminance (LT75) at 1000 cd/m^2.

used in OPVs.[67] However, there are relatively fewer reports in HyLEDs. Table 3 summarizes the performance of HyLEDs using solution-processed metal oxide/inorganic HTLs. As shown in the table, the lifetime data are rather limited, and more comprehensive studies are needed to understand the efficiency and lifetime of HyLEDs using solution-processed metal oxides.

3 Emitting Layers

Instead of a single-material based functional layer, most EMLs in most solution-processed OLEDs have a more complex host–guest system. The requirements for good host materials are stable film morphology, high triplet energy, bipolar charge transport properties, good solubility in solvents, and high glass transition temperature. Within the host–guest system, the luminescence quantum yield is also of concern. For more information about host–guest in EML, readers are referred to previous reviews focused on host materials in solution-processed small-molecule OLEDs.[88,89] The situation is different when another layer is subsequently processed on top of the small-molecule EML. In this section, the progress on making multilayer beyond EML is reviewed.

3.1 *Cross-Linkable EMLs*

Similar to HIL/HTL, cross-linkable materials offer an option for multilayer processing in EML. But the key issues associated with EMLs are exciton quenching by the initiators or byproducts, color shift due to exciplex formation, and change of recombination profiles. Following the early development of using CROP in X-HTLs, Rehmann et al.[90] turned the Ir-based emitter into a cross-linkable derivative (x-emitter). In multilayer solution-processed OLEDs, the previously reported X-HTL, namely *N,N′*-bis(4-(6-((3-ethyloxetan-3-y)methoxy)-hexyloxy)penyl-*N*, *N′*-bis(4-methoxyphenyl)biphenyl-4,4′-diamin, and *N,N′*-bis(4–(6–((3–ethyloxetan-3-y) methoxy))-hexylpenyl)-*N,N′*-diphenyl-4,4′-diamin (OTPD), was first spin cast as double HTLs.[13,48] The EML consisted of OTPD as the host and x-emitter as the guest; subsequently, the ETL was also solution processed with a mixture of 25% poly(methyl methacrylate) and 75% 2-(4-*tert*-butylphenyl)-5-biphenylyl-1,3,4-oxadiazole. The optimized device showed a maximum current efficiency of 18 cd/A. Ma et al.[57] incorporated two VB ethers to Ir emitter of red, green, and blue. The green and near-white multilayer OLED has an EQE of 8% and 2%, respectively. Aizawa et al. synthesized carbazole derivatives containing a VB group (DV-CBP)

and demonstrated an EQE of 2.3% in a solution-processed fluorescent OLED.[91] In contrast to adopting the chemistry from X-HTL to cross-linkable EML (X-EML), Volz et al.[92] demonstrated an autocatalyzed method to attach copper complexes to a polymer backbone, forming a cross-linked Cu-based EML. This strategy was used to enhance the electrochemical stability of the emitter materials.[92] The formation of the solvent-resistive cross-linking layer requires a high curing temperature which might damage the emitters. Another problem is that these cross-link-able side groups are generally insulating, resulting in low carrier mobilities in these cross-linked hosts or emitters. For X-EML prepared by CROP reaction, the existence of photoinitiators poses an additional problem of exciton quenching. Another approach to fabricate cross-linkable EMLs makes use of the electrochemical polymerization. Gu et al.[93] used sequentially electrochemical cross-linking to fabricate white OLEDs with a current efficiency of 5.5 cd/A. While this approach is interesting, there has not been follow up work done, suggesting the viability of this approach is questionable.

There is a paucity of reports on device stability in cross-linkable EML solution-processed OLEDs. The purity of OLED materials is a key factor determining the device operating stability. Among these cross-linkable EMLs, it is inevitable to introduce initiators or generate byproducts due to the cross-linking reaction. Thus, there are chemical species in the EML where charge transport and exciton formation occur. These impurities can serve as either charge traps or exciton quenching centers, degrading the device performance.

3.2 Orthogonal Material-Solvent Set for Combined EML/ETL

Several types of solvents can be employed to achieve orthogonal multilayer processing. One of the methods is to use fluorinated polymers and solvents. With sufficiently high fluorine content in the polymers, fluorinated polymers are soluble in fluorinated solvents but insoluble in common organic and aqueous/alcohol solvents. Fong et al. and Zakhidov et al. developed fluorinated light-emitting polymers and demonstrated a multilayer solution-processed PLED using red and green fluorinated EML stacks. The device can even be operated under chloroform immersion, showing the orthogonal solubility of fluorinated polymers.[94,95] However, owing to the fluorescent nature of polymer EMLs, the device efficiency of fluorinated PLEDs is significantly lower than that in phosphorescent OLEDs.

To incorporate phosphorescent emitters in multilayer solution-processed devices, polymer-based hosts, such as poly(N-vinylcarbazole) (PVK), are used as an EML in most solution-processed multilayer PhOLEDs.[88] During postannealing after solution process, polymer hosts form chain entanglement which might be able to withstand solvent wash from the subsequent layers. Most alcohol/water soluble ETLs can be processed on top of the polymer-based EML without dissolution. Since PVK is a hole-transporting host, most efficient OLEDs with PVK-based EML are incorporated with electron transporting molecules, such as 1,3-bis[2-(4-tert -butylphenyl)-1,3,4-oxadiazo-5-yl]benzene. Blue phosphorescent devices, which are solution processed from HIL up to the ETL, were demonstrated by Earmme et al.[96–99] with the ETLs processed via a mixture of formic acid and water (composition ratio 3:1). The highest EQE obtained was 19% for the FIrpic emitter and 16% for the $Ir(ppy)_3$ emitter. Huang et al.[100] reported a multilayer WOLED with solution-processed HTL, EML, and ETL. The ETL was prepared and spin cast in water/methanol solution and the overall device efficiency reached 14% EQE.[100]

One of the fundamental problems with the orthogonal solvent system approach is that small-molecule materials can be washed away by a solvent even though the small molecule might not be soluble in that solvent. For example, a small-molecule layer insoluble in alcohol solvents can still be washed away by the solvent during deposition of the subsequent layer even if an alcohol-based solvent is used. Recently, Aizawa et al.[101] demonstrated that if the molecular weight of the small molecule exceeds a certain threshold value, the film will remain intact. To illustrate this approach, they demonstrated that a higher molecular weight molecule (such as a dimer and trimer of a carbazole) has sufficient solvent resistance to 2-propanol used for the ETLs, whereas a carbazole monomer can easily be washed away by the same alcohol based solvent. With both dimers and trimers of carbazole as the host, they fabricated blue, green, and white OLEDs with a maximum EQEs of 20%, 22%, and 20%, respectively. This work opens up a route to fabricate small-molecule-based multilayer solution-processed OLEDs.

4 Electron Transport Layers

Since ETL is the last solution-processed layer before cathode deposition in an OLED of conventional structure, solvent resistance is usually not an issue with a thermally evaporated cathode. The requirements of solution-processed ETLs are high triplet energy for exciton confinement, good electron transport, proper energy level for electron injection and hole blocking, high glass transition temperature, high solubility ensuring film uniformity, and minimum processing damage to solution-processed EML.[4–6,102]

One of the approaches is to use water-/alcohol-based solvents where typical organic EML materials show very low solubilities. Huang et al.[103] has developed water/alcohol soluble conjugated polyelectrolytes (CPEs) for device fabrication,[103] and these materials have highly delocalized pi-conjugated main chains and polar pendant group substituted side chains.[104] CPEs can effectively modify the interface energy level, improve electron injection from the cathode and enable the use of air-stable metals with large work functions.[105,106] However, a delay between current switch-on and luminance turn-on was also observed. This is primarily attributed to the slow electrochemical nature of ionic transport. High-efficiency PLEDs with conjugated polyelectrolyte poly[9,9-bis(3′-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] as ETL and poly[2-(4-(3′,7′-dimethyloctyloxy)-phenyl)-p-phenylenevinylene] as EML were demonstrated with an EQE of 7.85%.[105] PLEDs with 10^5 fold enhancement of response time (to microseconds) was also reported by thermal and voltage treatments.[107] To date, there are only limited reports of high efficiency OLEDs using CPEs simultaneously with rapid response time. No work of CPEs applied in phosphorescent small-molecule OLEDs was reported. The major reason might be the lack of full-solvent orthogonality for small-molecule EMLs (as discussed in Sec. 3.2).

In addition to the polymer approach, Earmme et al.[96,97] have synthesized a series of small-molecule oligoquinolines ETLs that are compatible to formic acid/water-based solutions. Formic acid/water mixed solvents were utilized to process commercial ETLs, such as 4,7-diphenyl-1,10-phenanthroline and 1,3,5-tri(3-pyrid-3-yl-phenyl)benzene, and the devices showed an EQE of 19% in blue OLEDs.[98,99] Jiang et al.[108] reported diphenylphosphine oxide derivative for alcohol soluble ETL and the resulting multilayer white OLEDs yielded an EQE of 12%. Ye et al.[109] demonstrated mixed ETL in an alcohol/water solution, and a yellow OLED with such a mixed ETL showed an EQE of 13%.

Although high efficiencies are shown in the aforementioned solution-processed ETL devices, the solvents used for most ETL processing typically include water, which is problematic to device stability. Pu et al.[110] demonstrated a multilayer OLED employing zinc oxide (ZnO) as an ETL, thus minimizing the possibility of introducing water into devices. Multilayer solution-processed OLEDs using ZnO ETL showed a current efficiency of ~19 cd/A and a prolonged LT50 lifetime of more than 500 h at a luminance of 1200 cd/m². Currently, the concern of using ZnO as an ETL is the large electron injection barrier due to its deep EA (varying from −3.8 to −4.2 eV), which cannot match the lowest unoccupied molecular orbital energy of typical small-molecule hosts or emitters (ranging from −2.5 to −3.0 eV) in OLEDs, thereby limiting the device performance. Zhou et al.[111] used a polymer containing simple aliphatic amine groups, such as polyethyleneimine (PEI) to form a polymeric dipole layer, which serve as an interlayer modifying the work function of ZnO. Due to the presence of the interfacial dipole, the work function of the ZnO/PEI layer significantly decreased from 4.1 eV to 3.4 eV, which decreases the electron injection barrier into common organic EMLs. Therefore, this approach offers an option for ETL processed from a water-free solution, which is favorable for stable multilayer solution-processed OLEDs.

5 Concluding Remarks

In summary, we have reviewed different approaches to fabricate solution-processed multilayer OLEDs, including cross-linkable functional materials, orthogonal solvents, and inorganic functional materials. The use of cross-linkable materials enables wet processing which can withstand the subsequent solvent rinse. Common moieties for modifying HIL/HTL include oxetanes, styrenes, trifluorovinyl ethers, and BCB. However, cross-linking processes might lead to some

stability issues such as exciton quenching or charge traps. Further development of cross-linkable materials is needed to address the device stability issues.

Orthogonal solvent systems provide a means to process multilayer devices. Most reports of orthogonal solvent processing are actually based on high molecular weight polymers. There are few reports on small-molecule HTLs or EMLs compatible with orthogonal solvent processing. Small molecules can actually withstand multilayer processing as long as the molecular weight is higher than a critical value.[111] Currently, most HTL processing is based on organic solvents, whereas ETL processing (of either conjugated polyelectrolytes or small-molecule materials) is based on alcohol-/aqueous-based solvents. The introduction of water during processing is known to have detrimental effects on device stability and this is a fundamental issue that needs to be addressed in processing OLEDs based on orthogonal solvent systems.

Solution-processed metal oxide functional layers serve as an emerging alternative due to their insolubility in common solvents. OLEDs with NiO_x and MoO_3 HIL/HTL have been reported with high efficiencies. Additionally, OLEDs with ZnO ETL showed improved device stability. Because of the complexity of multilayer OLEDs, it is apparent that a combination of these approaches will be necessary to achieve high efficiencies and good stability OLEDs.

Acknowledgments

References

1. C. W. Tang and S. A. VanSlyke, "Organic electroluminescent diodes," *Appl. Phys. Lett.* **51**(12), 913–915 (1987).
2. M. A. Baldo, M. E. Thompson, and S. R. Forrest, "High-efficiency fluorescent organic light-emitting devices using a phosphorescent sensitizer," *Nature* **403**(6771), 750–753 (2000).
3. C. Adachi et al., "Nearly 100% internal phosphorescence efficiency in an organic light-emitting device," *J. Appl. Phys.* **90**(10), 5048–5051 (2001).
4. D. Tanaka et al., "Ultra high efficiency green organic light-emitting devices," *Jpn. J. Appl. Phys.* **46**(1L), L10 (2007).
5. H. Sasabe et al., "2-Phenylpyrimidine skeleton-based electron-transport materials for extremely efficient green organic light-emitting devices," *Chem. Commun.* (44), 5821–5823 (2008).
6. S.-J. Su et al., "Pyridine-containing triphenylbenzene derivatives with high electron mobility for highly efficient phosphorescent OLEDs," *Adv. Mater.* **20**(11), 2125–2130 (2008).
7. S.-J. Su et al., "Highly efficient organic blue-and white-light-emitting devices having a carrier- and exciton-confining structure for reduced efficiency roll-off," *Adv. Mater.* **20**(21), 4189–4194 (2008).
8. Y. Zheng et al., "Efficient deep-blue phosphorescent organic light-emitting device with improved electron and exciton confinement," *Appl. Phys. Lett.* **92**(22), 223301 (2008).
9. G. He et al., "High-efficiency and low-voltage p-i-n electrophosphorescent organic light-emitting diodes with double-emission layers," *Appl. Phys. Lett.* **85**(17), 3911–3913 (2004).
10. M. Ikai et al., "Highly efficient phosphorescence from organic light-emitting devices with an exciton-block layer," *Appl. Phys. Lett.* **79**(2), 156–158 (2001).
11. J.-W. Kang et al., "A host material containing tetraphenylsilane for phosphorescent OLEDs with high efficiency and operational stability," *Org. Electron.* **9**(4), 452–460 (2008).
12. J. H. Burroughes et al., "Light-emitting diodes based on conjugated polymers," *Nature* **347**(6293), 539–541 (1990).
13. X. Yang et al., "Highly efficient polymeric electrophosphorescent diodes," *Adv. Mater.* **18**(7), 948–954 (2006).
14. X. Gong et al., "High-efficiency polymer-based electrophosphorescent devices," *Adv. Mater.* **14**(8), 581–585 (2002).
15. X. H. Yang and D. Neher, "Polymer electrophosphorescence devices with high power conversion efficiencies," *Appl. Phys. Lett.* **84**(14), 2476–2478 (2004).

16. M. Cai et al., "High-efficiency solution-processed small molecule electrophosphorescent organic light-emitting diodes," *Adv. Mater.* **23**(31), 3590–3596 (2011).

17. H. Kim et al., "Small molecule based and solution processed highly efficient red electrophosphorescent organic light emitting devices," *Appl. Phys. Lett.* **91**(9), 093512 (2007).

18. J. Chen et al., "Solution-processable small molecules as efficient universal bipolar host for blue, green and red phosphorescent inverted OLEDs," *J. Mater. Chem.* **22**(11), 5164–5170 (2012).

19. Q. Fu et al., "Solution-processed single-emitting-layer white organic light-emitting diodes based on small molecules with efficiency/CRI/color-stability trade-off," *Opt. Express* **21**(9), 11078–11085 (2013).

20. L. Hou et al., "Efficient solution-processed small-molecule single emitting layer electrophosphorescent white light-emitting diodes," *Org. Electron.* **11**(8), 1344–1350 (2010).

21. L. Groenendaal et al., "Poly(3,4-ethylenedioxythiophene) and its derivatives: past, present, and future," *Adv. Mater.* **12**(7), 481–494 (2000).

22. G. H. C. Strack, "Clevios™ conductive, transparent and flexible polymers," 2015, http://www.heraeus-clevios.com/en/home/clevios-homepage.aspx (27 January 2015).

23. R. Po et al., "Polymer- and carbon-based electrodes for polymer solar cells: Toward low-cost, continuous fabrication over large area," *Sol. Energy Mater. Sol. Cells* **100**(0), 97–114 (2012).

24. C. Zhong et al., "Materials and devices toward fully solution processable organic light-emitting diodes," *Chem. Mater.* **23**(3), 326–340 (2011).

25. T.-W. Lee et al., "Hole-injecting conducting-polymer compositions for highly efficient and stable organic light-emitting diodes," *Appl. Phys. Lett.* **87**(23), 231106 (2005).

26. T. W. Lee et al., "Self-organized gradient hole injection to improve the performance of polymer electroluminescent devices," *Adv. Funct. Mater.* **17**(3), 390–396 (2007).

27. M.-R. Choi et al., "Polyaniline-based conducting polymer compositions with a high work function for hole-injection layers in organic light-emitting diodes: formation of ohmic contacts," *ChemSusChem* **4**(3), 363–368 (2011).

28. T.-H. Han et al., "Extremely efficient flexible organic light-emitting diodes with modified graphene anode," *Nat. Photonics* **6**(2), 105–110 (2012).

29. J. K. Park et al., "Electrophosphorescent devices with solution processible emitter and hole transport layer stack," *Curr. Appl. Phys.* **12**(Suppl 1), e38–e41 (2012).

30. T.-H. Han et al., "Molecularly controlled interfacial layer strategy toward highly efficient simple-structured organic light-emitting diodes," *Adv. Mater.* **24**(11), 1487–1493 (2012).

31. T. Giridhar et al., "An easy route to red emitting homoleptic IrIII complex for highly efficient solution-processed phosphorescent organic light-emitting diodes," *Chem.-Eur. J.* **20**(27), 8260–8264 (2014).

32. K. H. Yeoh et al., "The efficiency enhancement of single-layer solution-processed blue phosphorescent organic light emitting diodes by hole injection layer modification," *J. Phys. D Appl. Phys.* **47**(20), 205103 (2014).

33. M. Jaymand, "Recent progress in chemical modification of polyaniline," *Prog. Polym. Sci.* **38**(9), 1287–1306 (2013).

34. J. Jang, J. Ha, and K. Kim, "Organic light-emitting diode with polyaniline-poly(styrene sulfonate) as a hole injection layer," *Thin Solid Films* **516**(10), 3152–3156 (2008).

35. Y. Cao et al., "Solution-cast films of polyaniline: optical-quality transparent electrodes," *Appl. Phys. Lett.* **60**(22), 2711–2713 (1992).

36. A. De Girolamo Del Mauro et al., "Analysis of the performances of organic light-emitting devices with a doped or an undoped polyaniline–poly(4-styrenesulfonate) hole-injection layer," *J. Appl. Polym. Sci.* **122**(6), 3618–3623 (2011).

37. K. Fehse et al., "Combination of a polyaniline anode and doped charge transport layers for high-efficiency organic light emitting diodes," *J. Appl. Phys.* **101**(12), 124509 (2007).

38. M.-R. Choi et al., "Soluble self-doped conducting polymer compositions with tunable work function as hole injection/extraction layers in organic optoelectronics," *Angew. Chem.-Ger. Edit.* **123**(28), 6398–6401 (2011).

39. K. R. Choudhury et al., "Highly efficient hole injection using polymeric anode materials for small-molecule organic light-emitting diodes," *Adv. Funct. Mater.* **19**(3), 491–496 (2009).

40. S. Chen, X. Jiang, and F. So, "Hole injection polymer effect on degradation of organic light-emitting diodes," *Org. Electron.* **14**(10), 2518–2522 (2013).

41. E. Orselli et al., "Orange phosphorescent organic light-emitting diodes with high operational stability," *Org. Electron.* **13**(9), 1506–1510 (2012).

42. S. Ho et al., "Stable solution processed hole injection material for organic light-emitting diodes," *Org. Electron.* **15**(10), 2513–2517 (2014).

43. H.-W. Lin et al., "Solution-processed hexaazatriphenylene hexacarbonitrile as a universal hole-injection layer for organic light-emitting diodes," *Org. Electron.* **14**(4), 1204–1210 (2013).

44. C. A. Zuniga, S. Barlow, and S. R. Marder, "Approaches to solution-processed multilayer organic light-emitting diodes based on cross-linking," *Chem. Mater.* **23**(3), 658–681 (2011).

45. F. Huang et al., "Crosslinkable hole-transporting materials for solution processed polymer light-emitting diodes," *J. Mater. Chem.* **18**(38), 4495–4509 (2008).

46. A. Köhnen et al., "The simple way to solution-processed multilayer OLEDs – layered block-copolymer networks by living cationic polymerization," *Adv. Mater.* **21**(8), 879–884 (2009).

47. M. C. Gather et al., "Solution-processed full-color polymer organic light-emitting diode displays fabricated by direct photolithography," *Adv. Funct. Mater.* **17**(2), 191–200 (2007).

48. N. Rehmann et al., "Highly efficient solution-processed phosphorescent multilayer organic light-emitting diodes based on small-molecule hosts," *Appl. Phys. Lett.* **91**(10), 103507 (2007).

49. P. Zacharias et al., "New crosslinkable hole conductors for blue-phosphorescent organic light-emitting diodes," *Angew. Chem. Int. Edit.* **46**(23), 4388–4392 (2007).

50. M. C. Gather et al., "Highly-efficient solution-processed phosphorescent multi-layer organic light-emitting diodes investigated by electromodulation spectroscopy," *Appl. Phys. B* **95**(1), 113–124 (2009).

51. A. Pitarch, K. Meerholz, and D. Hertel, "Effect of dopant concentration on charge transport in crosslinkable polymers," *Phys. Status Solidi B* **245**(5), 814–819 (2008).

52. G. Liaptsis and K. Meerholz, "Crosslinkable TAPC-based hole-transport materials for solution-processed organic light-emitting diodes with reduced efficiency roll-off," *Adv. Funct. Mater.* **23**(3), 359–365 (2013).

53. G. Liaptsis, D. Hertel, and K. Meerholz, "Solution processed organic double light-emitting layer diode based on cross-linkable small molecular systems," *Angew. Chem.-Ger. Edit.* **125**(36), 9742–9746 (2013).

54. M. S. Liu et al., "Thermally cross-linkable hole-transporting materials for improving hole injection in multilayer blue-emitting phosphorescent polymer light-emitting diodes," *Macromolecules* **41**(24), 9570–9580 (2008).

55. Y. H. Niu et al., "Crosslinkable hole-transport layer on conducting polymer for high-efficiency white polymer light-emitting diodes," *Adv. Mater.* **19**(2), 300–304 (2007).

56. Y.-J. Cheng et al., "Thermally cross-linkable hole-transporting materials on conducting polymer: synthesis, characterization, and applications for polymer light-emitting devices," *Chem. Mater.* **20**(2), 413–422 (2008).

57. B. Ma et al., "Multifunctional crosslinkable iridium complexes as hole transporting/electron blocking and emitting materials for solution-processed multilayer organic light-emitting diodes," *Adv. Funct. Mater.* **19**(7), 1024–1031 (2009).

58. W. Jiang et al., "A high triplet energy small molecule based thermally cross-linkable hole-transporting material for solution-processed multilayer blue electrophosphorescent devices," *J. Mater. Chem. C* **3**(2), 243–246 (2015).

59. J. Park et al., "Facile photo-crosslinking of azide-containing hole-transporting polymers for highly efficient, solution-processed, multilayer organic light emitting devices," *Adv. Funct. Mater.* **24**(48), 7588–7596 (2014).

60. C. Xiang et al., "Phosphorescent organic light emitting diodes with a cross-linkable hole transporting material," *Org. Electron.* **15**(7), 1702–1706 (2014).

61. Y.-H. Niu et al., "Thermally crosslinked hole-transporting layers for cascade hole-injection and effective electron-blocking/exciton-confinement in phosphorescent polymer light-emitting diodes," *Appl. Phys. Lett.* **88**(9), 093505 (2006).

62. B. Ma et al., "New thermally cross-linkable polymer and its application as a hole-transporting layer for solution processed multilayer organic light emitting diodes," *Chem. Mater.* **19**(19), 4827–4832 (2007).

63. C. A. Zuniga et al., "Crosslinking using rapid thermal processing for the fabrication of efficient solution-processed phosphorescent organic light-emitting diodes," *Adv. Mater.* **25**(12), 1739–1744 (2013).

64. W. Li et al., "Covalently interlinked organic LED transport layers via spin-coating/siloxane condensation," *Adv. Mater.* **11**(9), 730–734 (1999).

65. H. Yan et al., "A polymer blend approach to fabricating the hole transport layer for polymer light-emitting diodes," *Appl. Phys. Lett.* **84**(19), 3873–3875 (2004).

66. J. Lee et al., "Utilization of "thiol-ene" photo cross-linkable hole-transporting polymers for solution-processed multilayer organic light-emitting diodes," *J. Mater. Chem. C* **2**(8), 1474–1481 (2014).

67. K. Zilberberg, J. Meyer, and T. Riedl, "Solution processed metal-oxides for organic electronic devices," *J. Mater. Chem. C* **1**(32), 4796–4815 (2013).

68. M. Sessolo and H. J. Bolink, "Hybrid organic–inorganic light-emitting diodes," *Adv. Mater.* **23**(16), 1829–1845 (2011).

69. J. Meyer et al., "Transition metal oxides for org. electron.: energetics, device physics and applications," *Adv. Mater.* **24**(40), 5408–5427 (2012).

70. D. Y. Kim et al., "The effect of molybdenum oxide interlayer on organic photovoltaic cells," *Appl. Phys. Lett.* **95**(9), 093304 (2009).

71. Irfan et al., "Energy level evolution of molybdenum trioxide interlayer between indium tin oxide and organic semiconductor," *Appl. Phys. Lett.* **96**(7), 073304 (2010).

72. Irfan et al., "Energy level evolution of air and oxygen exposed molybdenum trioxide films," *Appl. Phys. Lett.* **96**(24), 243307 (2010).

73. S. Chen et al., "Metal oxides for interface engineering in polymer solar cells," *J. Mater. Chem.* **22**(46), 24202–24212 (2012).

74. S. Höfle et al., "Molybdenum oxide anode buffer layers for solution processed, blue phosphorescent small molecule organic light emitting diodes," *Org. Electron.* **14**(7), 1820–1824 (2013).

75. L. Jian et al., "Aqueous solution-processed MoO_3 thick films as hole injection and short-circuit barrier layer in large-area organic light-emitting devices," *Appl. Phys. Express* **7**(11), 111601 (2014).

76. Q. Fu et al., "Room-temperature sol–gel derived molybdenum oxide thin films for efficient and stable solution-processed organic light-emitting diodes," *ACS Appl. Mater. Interfaces* **5**(13), 6024–6029 (2013).

77. G. Vida et al., "Characterization of tungsten surfaces by simultaneous work function and secondary electron emission measurements," *Microsc. Microanal.* **9**(04), 337–342 (2003).

78. S. Höfle et al., "Tungsten oxide buffer layers fabricated in an inert sol-gel process at room-temperature for blue organic light-emitting diodes," *Adv. Mater.* **25**(30), 4113–4116 (2013).

79. H. Choi et al., "Solution processed WO3 layer for the replacement of PEDOT:PSS layer in organic photovoltaic cells," *Org. Electron.* **13**(6), 959–968 (2012).

80. J. H. Youn et al., "Improving the lifetime of a polymer light-emitting diode by introducing solution processed tungsten-oxide," *J. Mater. Chem. C* **1**(19), 3250–3254 (2013).

81. J. Kim et al., "Solution processed polymer light emitting diode with vanadium-oxide doped PEDOT:PSS," *Phys. Status Solidi A* **212**(3), 640–645 (2015).

82. K. Zilberberg et al., "Inverted organic solar cells with sol-gel processed high work-function vanadium oxide hole-extraction layers," *Adv. Funct. Mater.* **21**(24), 4776–4783 (2011).

83. H. Lee, Y. Kwon, and C. Lee, "Improved performances in organic and polymer light-emitting diodes using solution-processed vanadium pentoxide as a hole injection layer," *J. Soc. Inf. Disp.* **20**(12), 640–645 (2012).

84. J. R. Manders et al., "Solution-processed nickel oxide hole transport layers in high efficiency polymer photovoltaic cells," *Adv. Funct. Mater.* **23**(23), 2993–3001 (2013).

85. S. Liu et al., "Nickel oxide hole injection/transport layers for efficient solution-processed organic light-emitting diodes," *Chem. Mater.* **26**(15), 4528–4534 (2014).

86. S. Liu et al., "Passivation of metal oxide surfaces for high-performance organic and hybrid optoelectronic devices," *Chem. Mater.* **27**(7), 2532–2539 (2015).

87. A. Perumal et al., "High-efficiency, solution-processed, multilayer phosphorescent organic light-emitting diodes with a copper thiocyanate hole-injection/hole-transport layer," *Adv. Mater.* **27**(1), 93–100 (2015).

88. K. S. Yook and J. Y. Lee, "Small molecule host materials for solution processed phosphorescent organic light-emitting diodes," *Adv. Mater.* **26**(25), 4218–4233 (2014).

89. W. Li, J. Li, and M. Wang, "Organic host materials for solution-processed phosphorescent organic light-emitting diodes," *Isr. J. Chem.* **54**(7), 867–884 (2014).

90. N. Rehmann et al., "Advanced device architecture for highly efficient organic light-emitting diodes with an orange-emitting crosslinkable iridium(III) complex," *Adv. Mater.* **20**(1), 129–133 (2008).

91. N. Aizawa et al., "Thermally cross-linkable host materials for enabling solution-processed multilayer stacks in organic light-emitting devices," *Org. Electron.* **14**(6), 1614–1620 (2013).

92. D. Volz et al., "Auto-catalysed crosslinking for next-generation OLED-design," *J. Mater. Chem.* **22**(38), 20786–20790 (2012).

93. C. Gu et al., "Multilayer polymer stacking by in situ electrochemical polymerization for color-stable white electroluminescence," *Adv. Mater.* **23**(4), 527–530 (2011).

94. H. H. Fong et al., "Orthogonal processing and patterning enabled by highly fluorinated light-emitting polymers," *Adv. Mater.* **23**(6), 735–739 (2011).

95. A. A. Zakhidov et al., "Orthogonal processing: a new strategy for organic electronics," *Chem. Sci.* **2**(6), 1178 (2011).

96. T. Earmme, E. Ahmed, and S. A. Jenekhe, "Solution-processed highly efficient blue phosphorescent polymer light-emitting diodes enabled by a new electron transport material," *Adv. Mater.* **22**(42), 4744–4748 (2010).

97. E. Ahmed, T. Earmme, and S. A. Jenekhe, "New solution-processable electron transport materials for highly efficient blue phosphorescent OLEDs," *Adv. Funct. Mater.* **21**(20), 3889–3899 (2011).

98. T. Earmme and S. A. Jenekhe, "Solution-processed, alkali metal-salt-doped, electron-transport layers for high-performance phosphorescent organic light-emitting diodes," *Adv. Funct. Mater.* **22**(24), 5126–5136 (2012).

99. T. Earmme and S. A. Jenekhe, "High-performance multilayered phosphorescent OLEDs by solution-processed commercial electron-transport materials," *J. Mater. Chem.* **22**(11), 4660–4668 (2012).

100. F. Huang et al., "Highly efficient polymer white-light-emitting diodes based on lithium salts doped electron transporting layer," *Adv. Mater.* **21**(3), 361–365 (2009).

101. N. Aizawa et al., "Solution-processed multilayer small-molecule light-emitting devices with high-efficiency white-light emission," *Nat. Commun.* **5**, 5756 (2014).

102. S.-J. Su et al., "Novel four-pyridylbenzene-armed biphenyls as electron-transport materials for phosphorescent OLEDs," *Org. Lett.* **10**(5), 941–944 (2008).

103. F. Huang, H. Wu, and Y. Cao, "Water/alcohol soluble conjugated polymers as highly efficient electron transporting/injection layer in optoelectronic devices," *Chem. Soc. Rev.* **39**(7), 2500–2521 (2010).

104. X. Cai et al., "Organometallic conjugated polyelectrolytes: synthesis and applications," *J. Inorg. Organomet. Polym.* **25**(1), 27–36 (2015).

105. H. Wu et al., "Efficient electron injection from a bilayer cathode consisting of aluminum and alcohol-/water-soluble conjugated polymers," *Adv. Mater.* **16**(20), 1826–1830 (2004).

106. H. Wu et al., "High-efficiency electron injection cathode of Au for polymer light-emitting devices," *Org. Electron.* **6**(3), 118–128 (2005).

107. A. Garcia et al., "Controlling ion motion in polymer light-emitting diodes containing conjugated polyelectrolyte electron injection layers," *J. Am. Chem. Soc.* **133**(8), 2492–2498 (2011).
108. W. Jiang et al., "Alcohol-soluble electron-transport small molecule for fully solution-processed multilayer white electrophosphorescent devices," *Org. Lett.* **16**(4), 1140–1143 (2014).
109. T. Ye et al., "Efficient phosphorescent polymer yellow-light-emitting diodes based on solution-processed small molecular electron transporting layer," *ACS Appl. Mater. Interfaces* **3**(2), 410–416 (2011).
110. Y.-J. Pu et al., "Fabrication of organic light-emitting devices comprising stacked light-emitting units by solution-based processes," *Adv. Mater.* **27**(8), 1327–1332 (2015).
111. Y. Zhou et al., "A universal method to produce low–work function electrodes for organic electronics," *Science* **336**(6079), 327–332 (2012).

Szuheng Ho received his BS degree from National Taiwan University, Taiwan, in 2010. He is currently pursuing his PhD in the Department of Materials Science and Engineering at the University of Florida. His research interests include fabrication and characterization of organic light-emitting devices.

Shuyi Liu received his BS degree in engineering from Tsinghua University, China, in 2010. He is currently pursuing his PhD in materials science and engineering. His research interests lie in solution processable organic and hybrid optoelectronic devices with emphasis on novel device architecture and fabrication methods.

Ying Chen is a postdoctoral researcher in the Material Science and Engineering Department at the University of Florida. He received his PhD in physics from Iowa State University. His research focuses on the study of organic semiconductor device physics and fabrication of high performance organic light-emitting diodes.

Franky So received his PhD in electrical engineering from the University of Southern California. He is currently the Rolf E. Hummel professor of electronic materials in the Department of Materials Science and Engineering at the University of Florida. His current areas of research interest include organic-based and quantum dot optoelectronic devices. He is a fellow of SPIE, IEEE, and OSA. He is also a distinguished lecturer of the IEEE Photonics Society.