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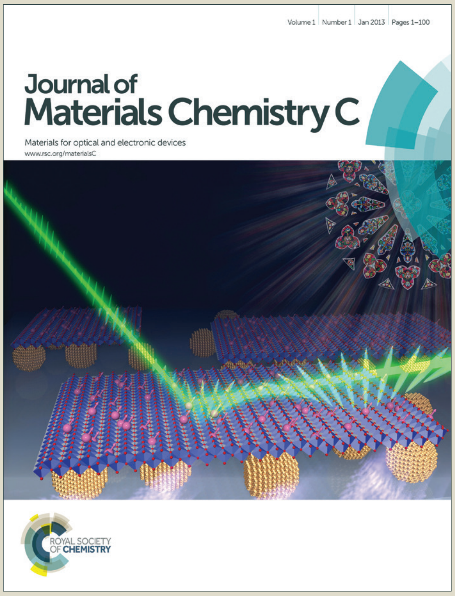

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Solution-Processable Electron Injection Materials for Organic Light-Emitting Devices

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Abstract

Solution-processed organic light-emitting devices (OLEDs) have been progressed as a potential candidate for cost-effective solid-state lighting and flat panel displays. In this highlight, we focus on the recent progress of the state-of-the-art solution-processable electron injection materials: i) alkali metal-containing compounds, ii) *n*-type semiconducting metal oxides, iii) π-conjugated ionic polymers, and iv) nonionic polymers. These materials are soluble in water, alcohol, or a water-alcohol mixture solvent and can be formed to a film by a solution process. We discuss essential characteristics of these electron injection materials and the performance of the solution-processed OLEDs made with them.

1. Introduction

Novel materials and device architecture have been developed to improve the performance of organic light-emitting devices (OLEDs).[1-15] The conventional device structure of OLEDs consists of multiple layers of several functional organic materials, including the hole injection layer (HIL), hole transporting layer (HTL), emitting layer (EML), electron transporting layer (ETL), and electron injection layer (EIL), placed between a transparent indium tin oxide (ITO) anode and a reflective metal cathode, as shown in Figure 1(a). Multilayer OLEDs are generally fabricated by the thermal evaporation process in vacuum. However, vacuum thermal evaporation process carries a high manufacturing cost, especially for large-area devices. On the other hand, solution-processed techniques used in the fabrication of OLEDs, such as spin coating, slot die coating, inkjet coating, and roll-to-roll coating have been considered to be advantageous to reduce fabrication costs.[16-18] However, the fabrication of fully solution-processed OLEDs, except the electrode, is not straightforward because the coating solvent of an organic layer usually dissolves the underlayer and these two layers become mixed. Therefore, orthogonal solvents that dissolve a coating upper layer but do not dissolve a coated underlayer[19, 20], and cross-linking processes that make a coated underlayer insoluble[21, 22], are key feature to achieve solution-processed multilayer OLEDs.

EILs, described in this Highlight, have an important role in OLEDs to facilitate electron injection from a metal cathode into electron transporting materials or light-emitting materials, reduce driving voltage, and improve power efficiency (lm/W). Energy-level alignment between an organic layer and a metal electrode for electron injection has been achieved with the EIL of alkali metals such as Li, Ca, or Ba, and alkali metal halides such as LiF, NaF, or CsF.[23-28] However, these EILs cannot naturally be adapted for solution processing because of their insolubility to common organic solvents. Therefore, to achieve solution-processing of electron injection materials, they should have several properties, including not only electron injection ability but also solubility to coating solvents and film-forming ability. When electron injection materials are spin-coated onto EML in the conventional OLED structure (Figure 1(a)), water/alcohol solvent are usually employed for the EIL as a poor solvent to the EML, preventing dissolution of the EML consisting of π-conjugated light-emitting polymers or relatively high molecular weight small molecules.[19, 20] The solubility of the EIL to the coating solvent and the insolubility of the EML are essential to fabricate solution-processed multilayer OLEDs. First report of solution-processed EIL is the use of sodium sulfonated polystyrene for polymer light-emitting devices (PLEDs).[29] Inorganic alkali metal salts, cesium carbonate (Cs_2CO_3), was also reported as solution-processed EIL in PLEDs.[30, 31]

In the inverted type of device structure, where ITO is used as a cathode and reflective metal is used as an anode, the electron injection materials are coated onto the ITO cathode. For inverted OLEDs (Figure 1(b)), the EIL materials themselves have to be insoluble to the coating solvent of the upper layer, but various solvents other than water/alcohol can be used for the EIL coating itself because of the insolubility of ITO. In addition, the annealing temperature of the EIL on ITO in the inverted OLEDs can be much higher than that of the EIL in the regular-structure OLEDs. Because of this reduced restriction of the EIL coating condition, the inverted structure has tended to be preferred in OLEDs with solution-processed EIL.

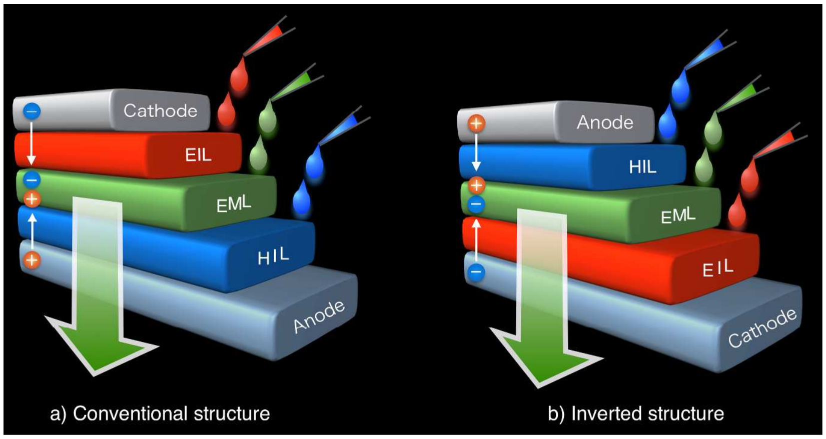


Figure 1. a) Conventional structure and b) inverted structure of solution-processed OLEDs.

In this highlight, we classify solution-processable EIL materials into four categories. First, alkali metal-containing compounds such as cesium carbonate, cesium stearate and lithium phenolate complexes are described, for replacement of the low-work-function alkali metals. Second, *n*-type semiconducting metal oxides such as titanium oxide (TiO_2) and zinc oxide (ZnO) are described. Polyethyleneimine forms strong dipoles on the metal oxide or metal electrode, reducing their work function and improving their electron injection. Third, we describe alcohol/water-soluble ionic π-conjugated polymers, zwitterionic polyelectrolytes, and nonconjugated ionic polymers, directly spin-coated onto EML. Fourth, we describe a polymer binder dispersing alkali metal salts or metal oxides, improving the roughness and conductivity of the film. Chemical structures of the materials are shown in Figure 2.

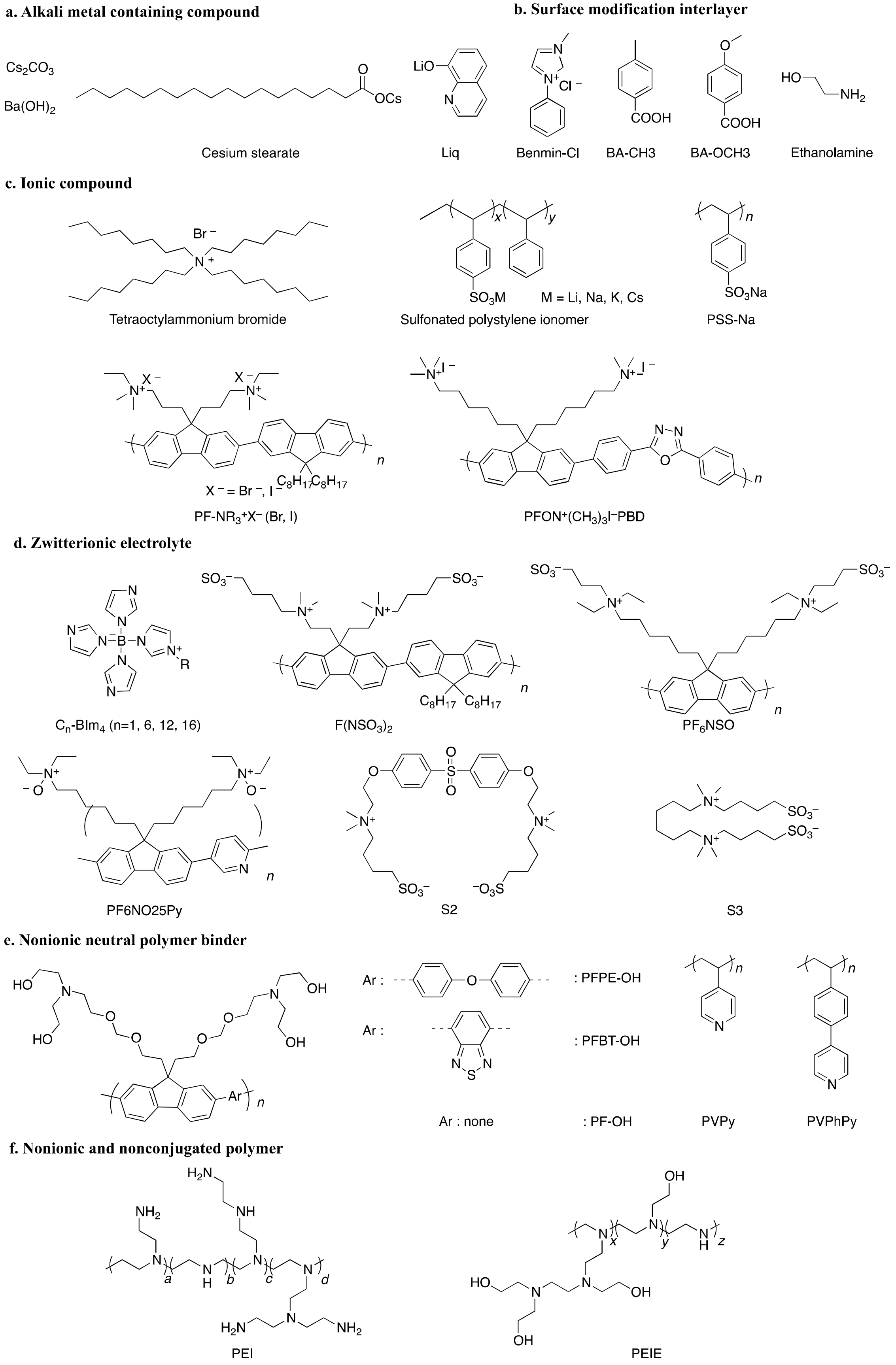


Figure 2. Chemical structures of the solution-processable EIL materials.

2. Alkali Metal-Containing Compounds

In the π-conjugated light-emitting polymer OLEDs, low-work-function metals such as calcium and barium are used as the EIL.[32, 33] However, these alkali metals and their compounds are insoluble in common organic solvents such as toluene, *p*-xylene, chlorobenzene, tetrahydrofuran, and alcohols. Thus, these low-work-function metals cannot be applied for solution-processed OLEDs. In addition, these metals are highly reactive and unstable in air. Recently, Cs_2CO_3[30, 31], cesium stearate[34], and lithium phenolate complexes[35] have been used as solution-processable EIL materials because they are soluble in alcohols such as 2-ethoxyethanol and 2-methoxyethanol. Thus, these alkali metal-containing materials can be spin-coated onto EML from an alcohol solution without dissolution of the underlayer, and exhibit the same superior electron injection properties as low-work-function metals. Solution-processed Cs_2CO_3 ultrathin film is inserted between the metal cathode and a conventional light-emitting polymer such as poly(9,9-dioctylfluorene) (PFO), poly(9,9-dioctylfluorene-*alt*-benzothiadiazole) (F8BT), or poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV), and improves electron injection into the polymer layer and hole blocking from the polymer layer, resulting in improved charge balance and high efficiencies.[30, 31] UV photoelectron spectroscopy (UPS) measurement of spin-coated Cs_2CO_3 film on which aluminum (Al) was evaporated showed a low work function of 2.8 eV and reduced electron injection barrier, shown in Figure 3. This result indicates that a reaction between spin-coated Cs_2CO_3 and thermally evaporated Al forms an Al-O-Cs complex and leads to reduction of the cathode work function.

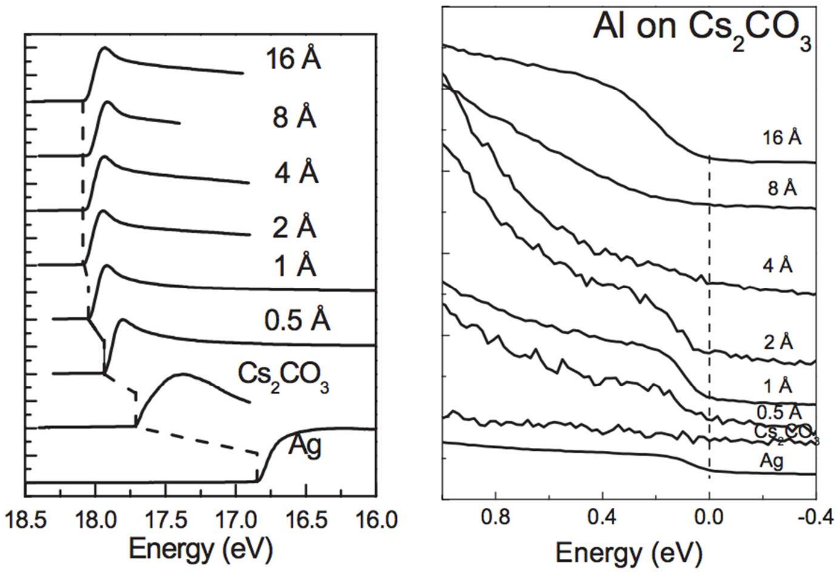


Figure 3. UPS spectra of solution-processed Cs_2CO_3 before and after the deposition of Al. Reprinted with permission from Ref. 31. Copyright 2007 WILEY-VCH.

Cs_2CO_3 is also used as an *n*-type dopant for electron transport materials to improve the conductivity and operational voltage. These doping methods, such as chemical doping, have been developed for a long time for thermal evaporated small molecular-based OLEDs.[36-39] In contrast, solution-processed *n*-type chemical doping methods are less reported. Jenekhe et al. reported that solution-processed electron transport materials, 1,3,5-tris(*m*-pyrid-3-yl-phenyl)benzene (TmPyPB), doped with Cs_2CO_3, was spin-coated from a formic acid/water solvent onto the EML. This polar mixture solvent does not dissolve the EML, and thus a solution-processed multilayer structure can be fabricated without dissolving the underlayer. High current efficiency of 37.7 cd/A and an external quantum efficiency (EQE) of 19% at a high luminance were achieved in blue phosphorescent OLEDs.[40]

Cesium stearate is designed and synthesized for replacement of Cs_2CO_3 to improve solubility, increasing the solvent options. The long alkyl chain of cesium stearate makes the molecule soluble in ethanol and it can be spin-coated from solution onto EML.[34] Solution-processed cesium stearate as an EIL exhibited ohmic contact and and almost identical electron injection property to that of conventional devices with evaporated barium as EIL in orange and blue light-emitting polymer OLEDs. In this case, cesium stearate was effective for not only the relatively deep lowest unoccupied molecular orbital (LUMO) level of the orange light-emitting polymer (2.7 eV) but also even the shallow LUMO level of the blue light-emitting polymer (2.1 eV). However, alkali metal carbonate salts e.g. Cs_2CO_3, Li_2CO_3, and Na_2CO_3 have disadvantages such as their high hygroscopicity in air. On the other hand, lithium complexes with a phenolate ligand are stable and less hygroscopic in air than alkali metal carbonate salts.[35] Moreover, Liq is soluble in various alcohols such as methanol, ethanol, isopropanol, and 2-ethoxyethanol, and can be spin-coated as a smooth thin film onto EML. Solution-processed Liq as an EIL for F8BT in OLEDs exhibits lower driving voltage of 3.5 V at 1000 cd m^{-2}, compared with spin-coated Cs_2CO_3 and thermal evaporated calcium. To investigate air stability of Liq and Cs_2CO_3, their films were exposed to air for 30 min after spin-coating onto F8BT in nitrogen atmosphere, before evaporation of the Al cathode. The device with air-exposed Liq exhibited less driving voltage shift than that with air exposed Cs_2CO_3. The device with the air-exposed Liq exhibited a stable clear emission image, but the device with Cs_2CO_3 showed a large number of defects in the emission image because of the influence of moisture.

3. Metal Oxides

Solution-processed metal oxides such as TiO_2[41-43], ZnO[35, 43-47], and ZrO_2[48] have recently been reported as electron injection materials in OLEDs because of their high stability to moisture and oxygen. Their excellent optoelectrical properties, e.g., mobility and transparency, are suitable for application to OLEDs. The thin film of these metal oxides can be formed by various solution-process methods. Metal oxide thin films deposited by sol-gel methods have been applied in the inverted device configuration, which consists of the ITO cathode and a stable metal anode such as Au or Ag. Another method is deposition of the metal oxide nanoparticles that are easily synthesized from a precursor of metal oxide such as zinc acetate in alcohols under basic conditions. The synthesized metal oxide nanoparticles can be dispersed into alcohol solvents. The advantage of this method is that a high-temperature annealing process is not required, unlike with conventional sol-gel methods, and the metal oxides can be coated onto the EML with a conventional device structure.

TiO_2 has been highly important because of its chemical stability, high conductivity, wide energy gap, high transparency and inexpensive material cost. The conduction band (CB) of TiO_2 is approximately 3.8 eV, close to the LUMO level of π-conjugated light-emitting polymers in OLEDs. Solution-processed TiO_2 as an EIL in the inverted type of OLED based on the light-emitting polymer F8BT was fabricated to replace low-work-functional metals.[41] A thin film of TiO_2 was deposited onto a fluorine-doped tin oxide (FTO) glass substrate by spray pyrolysis using an ethanol solution of titanium diisopropoxy bis(acetylacetonate), and then annealed at 450 °C. The device with TiO_2 showed higher stability in air compared with a conventional device using a calcium EIL.

Titanium sub-oxide (TiO_x) was also used as an air-stable EIL on top of a light-emitting polymer (Super Yellow) in the conventional device structure to prevent penetration of oxygen and moisture into the polymer layer.[42] In this method, the precursor solution is commonly prepared by mixing titanium isopropoxide and ethanolamine. The spin-coated film is annealed for 15 h at a relatively low temperature of 150 °C to be converted to TiO_x by hydrolysis reaction. Luminance-voltage characteristics of the device with TiO_x showed high stability in air compared with the device without TiO_x. These results suggest that the 30 nm-thick TiO_x layer plays a role in the oxygen blocking effect as well as the electron injection property.

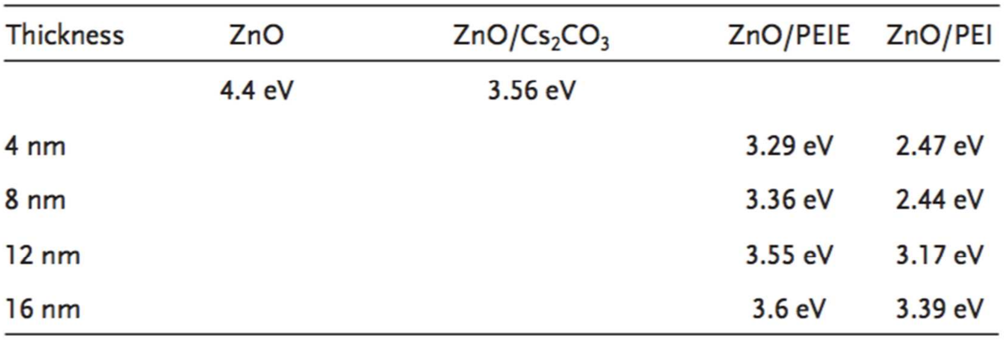
Solution-processed ZnO film is widely used as an EIL in the inverted OLED configuration because of the energy level matching with the CB of ZnO (approximately 4 eV) and the LUMO level (3–2.5 eV) of conventional π-conjugated light-emitting polymers.[44] In general, compact thin ZnO films have been deposited by the spray pyrolysis technique. The zinc acetate precursor solution is sprayed onto an ITO glass substrate, and subsequently annealed at a high temperature of 400–500 °C for a few hours. The inverted-type polymer OLED with ZnO film as an EIL and MoO_3 as an HIL exhibited superior efficiencies compared to the conventional device with PEDOT:PSS as an HIL and barium as an EIL. In addition, the inverted device with ZnO also shows higher luminance and efficiency, and lower driving voltage, compared to the device with TiO_2 as an EIL, although the energy levels of ZnO and TiO_2 are similar.[43] This result is attributed to the difference in the surface polarity. The presence of Zn ions at the ZnO surface is estimated to cause a superior electron injection property, improving efficiency. Moreover, the photoluminescence quantum yield (PLQY) of TiO_2/F8BT is lower (65%) than that of F8BT film (77%) film and ZnO/F8BT (75%) because of the exciton-quenching effect of TiO_2.

ZnO nanoparticles (NPs) can also be applied to a solution-processed EIL in the inverted and conventional device configurations[35, 45-47]; various synthesis methods of ZnO NPs have been reported. Dropwise addition of a stoichiometric amount of tetramethylammonium hydroxide (TMAH) in ethanol into zinc acetate dihydrate in dimethyl sulfoxide (DMSO), followed by stirring for 1 h, forms the ZnO with a size of 2–3 nm.[45] Poly(p-phenylene vinylene) (PPV)–based conventional configuration OLEDs with ZnO NPs as an EIL exhibited extremely low turn-on voltage, less than the optical band gap of the light-emitting PPV polymer. This result was explained by an Auger-assisted energy up-conversion process at the interfaces of PPV/ZnO. In another method of ZnO NP synthesis, zinc acetate and potassium hydroxide (KOH) are mixed together into a methanol solution with reflux for a few hours.[35, 47] Precipitated ZnO NPs with a particle size of 8 nm are dispersed into 2-ethoxyethanol with a concentration of 10 mg/ml after washing several times by methanol. With the ZnO NPs as an EIL, F8BT-based PLEDs showed a high luminance of more than 10,000 cd/cm^2 at 7 V.[35]

The energy barrier between the CB of ZnO (4 eV) and the LUMO of the light-emitting polymers (2–3 eV) is relatively large. Several approaches have been explored to improve electron injection from the ZnO into the light-emitting polymers by surface modification of the ZnO with Cs_2CO_3[49-52], or barium hydroxide ($Ba(OH)_2$), and others[53]. The device with ZnO/$Ba(OH)_2$ shows higher efficiency than those of ZnO/Cs_2CO_3 because of the reduction of exciton quenching at the Al cathode. In addition, an ionic liquid molecule (ILM) such as 1-benzyl-3-methylimidazolium chloride (benmim-Cl)[54] and a self-assembled dipole monolayer (SADM) such as methylbenzoic acid (BA-CH_3) and methoxybenzoic acid (BA-OCH_3)[55], tetra-n-butylammonium tetrafluoborate ($TBABF_4$)[46], cationic polymer of poly(9,9′-bis(6″-N,N,N-trimethylammoniumhexyl)fluorene-co-alt-phenylene) with bromide counterions (FPQ-Br)[56], are also used as surface modification layers for ZnO. These materials cause the formation of a strong dipole on the ZnO, which remarkably reduces the electron injection barrier between the CB of ZnO and the LUMO level of the light-emitting polymers.

Recently, air-stable nonionic and nonconjugated polyethyleneimine (PEI) and polyethyleneimine ethoxylated (PEIE) have been widely used as an EIL for inverted or regular OLED configurations.[57-62] The PEI and PEIE comprise an aliphatic amine backbone and amine or hydroxyl side chain group. They form not only an intermolecular dipole moment but also a dipole with electrodes such as ITO[57-59], gold (Au)[58], silver (Ag)[58, 60], Al[58], and PEDOT:PSS[58]. These strong dipole moments can dramatically reduce the work function of the electrode and electron injection barrier because of the vacuum level shift. The ZnO covered with PEI or PEIE exhibited a great reduction of work function of 2–3 eV compared with the ZnO without PEI or PEIE (Table 1).[58, 61, 62] These work function shifts are larger than the ZnO with Cs_2CO_3. These surface modification materials for ZnO are becoming a widely used useful methods to improve electron injection in the solution-processed inverted OLEDs.

Table.1 Work function of ZnO and ZnO with Cs_2CO_3, PEIE and PEI. Reprinted with permission from Ref. 61. Copyright 2014 WILEY-VCH.



Thickness	ZnO	ZnO/Cs_2CO_3	ZnO/PEIE	ZnO/PEI
	4.4 eV	3.56 eV		
4 nm			3.29 eV	2.47 eV
8 nm			3.36 eV	2.44 eV
12 nm			3.55 eV	3.17 eV
16 nm			3.6 eV	3.39 eV

The ripple-shaped nanostructure of ZnO (ZnO-R) is reported to exhibit the enhancement of light extraction efficiency due to improvement of waveguide modes, compared with flat film of ZnO (ZnO-F) as shown in Figure 4.[63] In addition to the light outcoupling enhancement, the treatment of the ZnO layer with amine-based polar solvent leads to reduction of the electron injection barrier and exciton quenching. The resulting current efficiency of 60 cd/A and external quantum efficiency of 17% were obtained in solution-processed polymer OLEDs.

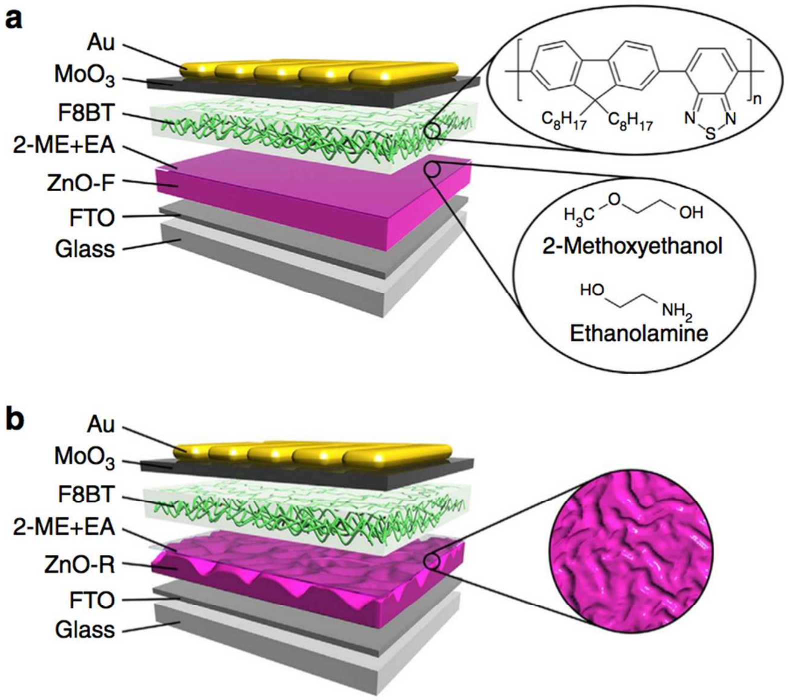


Figure.4 Device structure of an inverted OLEDs with amine-based solvent-treated ZnO as a surface modification layer. Reprinted with permission from Ref. 63. Copyright 2014 Nature Publishing Group.

4. Ionic Polymer and Small Molecular Material

Various water/alcohol soluble polymers such as π-conjugated polyelectrolytes[64-69], small molecular ionic material[70, 71], zwitterionic materials[72-76], and nonconjugated polymers[77, 78] have been applied to ETLs or EILs in solution-processed OLEDs. These polymers contain polar groups in the backbone or side chain, which are causes of high solubility in water/alcohols. The water/alcohol polar solvents do not dissolve conventional light-emitting polymers, and thus those water/alcohol soluble polymers can be spin-coated onto light-emitting polymers as an efficient EILs.

Most π-conjugated polymer electrolytes consist of a fluorene-based polymer backbone and ionized alkyl pendant groups with mobile counterions such as I-, Br-[64-66], and tetrasubstituted borates (BIm_4^-)[69]. In particular, PF-$NR_3^+X^-$ (Br, I)[64] and PFON$^+$(CH_3)$_3$I$^-$–PBD[66] were applied for blue, green, and red OLEDs as efficient ETLs and EILs. Small molecular ionic materials, tetraoctylammonium bromide (TOAB),[70] and triphenylsulfonium (TPS) salts[71] were also used as EILs in solution-processed OLEDs. These π-conjugated polyelectrolytes and small molecular ionic materials also cause dipole formation between the light-emitting layer and cathode, and improve electron injection properties.[68-71] However, the devices with ionic EILs cause concern because of the migration of mobile counterions into light-emitting polymer, which causes exciton quenching. In addition, luminance response time of the device with the π-conjugated polyelectrolyte is delayed by an ion mobile.

Zwitterionic polyelectrolytes containing conjugated backbone and zwitterionic side chain without free counterions have also been reported as efficient EILs for solution-processed OLEDs. Various zwitterioncic substituents such as sodium tetrakis(1-imidazolyl)borate (C_n–BIm_4)[72], sulfoammonium ($F(NSO_3)_2$[73], PF_6NSO[74]), and amine *N*-oxide (PF6NO25Py)[75] are applied to neutral and conjugated polymers. In particular, the performances of a device with $F(NSO_3)_2$ and PF6NO25Py showed higher luminance and current efficiency than that of a device with Ca or Ba as an EIL. The improvement of the electron injection is due to the formation of strong dipole alignment between the zweitterionc polymer and Al cathode and reduction of the electron injection barrier. Small molecule zwitterionic materials such as S2 and S3[76] exhibit superior electron injection properties as well as the polyelectrolytes as shown in Figure. 5. These results indicate that the small molecule zwitterionc materials are also effective as an EIL even with a nonconjugated structure. The zwitterionic polymers or small molecule electrolytes for EILs have an advantage of high response time of luminance (approximately 10 μs) compared with the conventional ionic polymers.

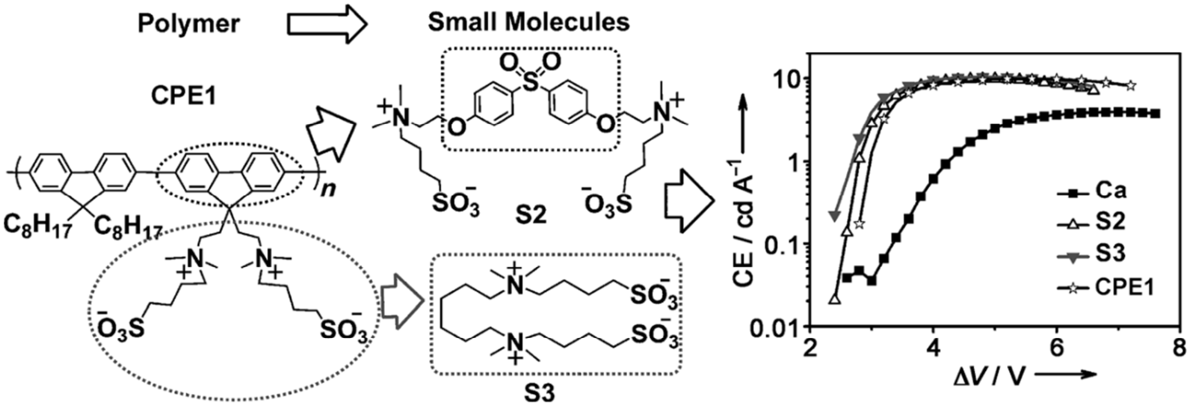


Figure 5. Structure of the conjugated polyelectrolyte (CPE1) and the small molecule zwitterionic materials (S2 and S3) with the current efficiency of the devices. Reprinted with permission from Ref. 76. Copyright 2013 WILEY-VCH.

Nonconjugated anionic polyelectrolytes, poly(sodium 4-styrenesulfonate) (PSS-Na)[29, 77, 78], are also used as EILs in OLEDs. The device with a thin PSS-Na layer exhibited lower driving voltage and higher efficiencies compared to a device with thermal evaporated LiF.

5. Nonionic polymers

Alcohol-soluble nonionic conjugated polymers have also been developed for electron transport and injection layers in fluorescent and phosphorescent OLEDs.[79-83] These neutral conjugated polymers such as poly[9,9-bis(2-(2-(2-diethanolaminoethoxy) ethoxy)ethyl)fluorene] (PF-OH) and their derivatives (PFPE-OH, PFBT-PH) are highly soluble even in methanol and exhibit high electron injection properties as well as ionic π-conjugated polymers and zwitterionic electrolytes. The neutral conjugated polymers do not have mobile ions in the compounds, and are not considered to affect the device operation. PF-OH was used as an *n*-type host material with alkali metal salts such as Li_2CO_3, and improved electron transport characteristics.[80] Solution-processed white phosphorescent OLEDs with PF-OH doped with Li_2CO_3 showed high current and power efficiency of 36 cd/A and 23 lm/W. Similarly, nonionic poly(ethyleneoxide) (PEO) have been employed as a host polymer blended with alkali metal salts such as Cs_2CO_3[81], KCF_3SO_3[82], and ionic sodium dodecyl sulfate (SDS)[83]. These mixed EILs improved not only efficiency but also stability to oxygen and moisture.

The alkylamine-based polymers, PEI and PEIE, themselves were used as EIL without ZnO, directly spin-coated onto light-emitting polymers.[60] Large work function shits of 1.5 eV for PEI/Ag and 1.3 eV for PEIE/Ag were observed with the amine polymer thicker than 5 nm. The devices with PEI/Ag and PEIE/Ag exhibited a comparable efficiency to the device with low work functional Ca as an EIL. In addition, large number of dark spots were observed in the device with Ca EIL, whereas the devices with PEI and PEIE exhibited less dark spots four weeks after the device fabrication because of high stability of PEI and PEIE in air.

A series of poly(vinylpyridine) (PVPy) and poly(vinylphenylpyridine) (PVPhPy) are reported as polymer binders mixed with Liq, exhibiting good electron transport and injection properties.[84] Mixing the binders with Liq improved the driving voltage characteristics of the device even with a relatively large thickness (16 nm) of the mixed EILs. The improvement presumably resulted from the interaction of the pyridine rings and the Li atom of Liq. The thick EIL is expected to be advantageous for large-scale coating with a solution process because it is difficult to simultaneously manage both a large area and a uniformly small thickness of a few nm, at the same time. The polymer binder also improves the film morphology.[47] The spin-coated film of the ZnO nanoparticles shows a high surface roughness due to agglutination of the nanoparticles. The addition of PVPy into the ZnO nanoparticles dramatically reduced film roughness without impairing the device efficiencies, although PVPy is an insulating material, as shown in Figure 6. The addition of the polymer binder into ZnO is an effective method to achieve morphology control and improvement of electron injection properties simultaneously.

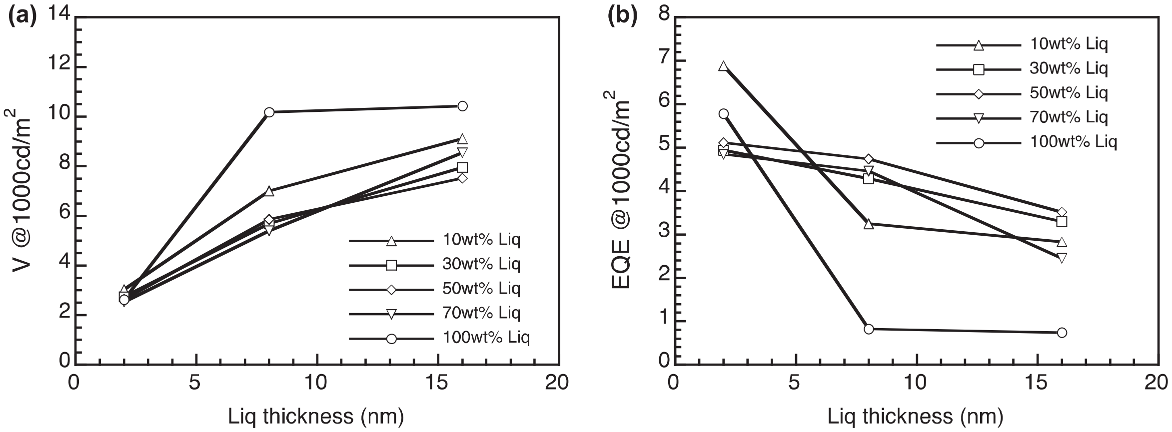


Figure 6. OLED performance as a function of the thickness of PVPhy:Liq. (a) driving voltage and (b) external quantum efficiency. Reprinted with permission from Ref. 84. Copyright 2014 WILEY-VCH.

6. Summary and outlook

Solution-processed OLEDs have been developed for large-area printing processes and low production costs in the past decade. The key feature to achieve high efficiency by the solution-processing method is the fabrication of multilayer structure as effectively as dry-processed OLEDs. Consequently, a number of researchers have focused on the solution-processed multilayer structure using various approaches such as cross-linking methods or orthogonal solvents techniques; the two-layer structure of HIL/EML and three-layer structure of HIL/HTL/EML or HIL/EML/ETL have been reported. Recently, a highly efficient four-layer structure, HIL/HTL/EML/ETL, of small-molecule-based OLEDs was achieved by the solution-processing method, in which their efficiencies are comparable to those of vacuum evaporated OLEDs. However, solution-processing of electron injection materials for multilayer OLEDs has remained a very complicated issue; it requires several properties such as solubility to a coating solvent, insolubility of the underlayer to the coating solvent, film-forming property, and electron injection ability.

In this highlight, we focused our attention on various solution-processable electron injection materials for OLEDs: alkali metal-containing compounds, *n*-type metal oxide, ionic polymer/small-molecule, zwitterionic polymer/small-molecule, and air-stable nonconjugated and nonionic polymers. The materials soluble in water/alcohol solvents have been employed for i) conventional structure of the device with π-conjugated polymers as an EML because of their insolubility to alcohol solvents, and ii) inverted device structures in which the EILs can be directly spin-coated onto the bottom electrodes (cathode) with a substrate.

Alkali metal-containing compounds such as Cs_2CO_3, cesium stearate, and lithium phenolate complexes of Liq have been used as efficient solution-processable EILs to replace the low-work-function metals such as Ca and Ba. Cs_2CO_3 is dissolved in higher alcohols such as 2-ethoxythanol and 2-methoxyethanol. Cesium stearate is soluble even in ethanol and its solubility is higher than the solubility of Cs_2CO_3. Similarly, Liq is also soluble in a wide range of alcohols. These alcohol-soluble alkali metal-containing compounds can be applied to the solution process as spin-coating onto an EML. Generally, thickness of alkali metal-containing compounds as an EIL needs to be ultrathin below 2 nm because of their poor electron transportability. However, precise control of EIL thickness with ultrathin layer is extremely difficult in large-scale solution processing. Thus, relatively thick layer (20 nm) of electron injection materials is required for solution-processed large-scale device.

The sol-gel method of *n*-type metal oxides such as TiO_2 and ZnO have been employed especially for inverted-structure of OLEDs because high-temperature annealing of the oxides is possible on a glass substrate. ZnO nanoparticles can be dispersed into alcohols and used in the fabrication of conventional-structure OLEDs. Additionally, surface modification materials for ZnO, such as Cs_2CO_3, ILM, SADM, and amine-based materials have been demonstrated to improve electron injection from the ZnO into the light-emitting polymer from the cathode. These results are attained forming a strong dipole causes a reduction of the electron injection barrier. Nanostructure modification of ZnO also cause the enhancement of light extraction efficiency due to improved waveguide modes compared with standard flat ZnO film. These several modification methods of ZnO layer have been adapted only for the inverted device configuration with π-conjugated fluorescent light-emitting polymer.

Water/alcohol soluble polymers, such as ionic π-conjugated polymers or ionic small molecules, containing polar groups with mobile counterion in the backbone or side chain, have been applied to ETLs and EILs with relatively thick thickness (10-20 nm) for solution-processed multilayer OLEDs. Using zwitterionic polymers/small-molecules has the advantage of less exciton quenching and high response of luminance, due to the free mobile counterions. The electron injection property and efficiency of the OLEDs using these ionic materials for EILs are comparable to those of Ca and Ba. Various nonionic polymers are useful as an *n*-type host material with alkali metal-containing compounds. Pyridine-containing polymers are useful as a binder for improving film roughness, and they can accept thickness variation of several nm.

Most recently, solution-processed tandem OLEDs have been reported by the use of ZnO and amine-based polymers as not only an EIL but also a solvent-blocking layer. The multilayer of ZnO and amine-based polymer can prevent the penetration of the upper coating solvent into the underlayer. Thus, an additional layer can be coated onto the amine-modified ZnO layer without dissolving the organic underlayer. From this viewpoint, the controlled solubility of EILs, especially used in a bottom light-emitting unit, is a key component for fabricating a tandem structure from the solution process**.**

Finally, solution-processed small molecule phosphorescent OLEDs have a great deal of attention due to their high efficiency and low power consumption in recent years. However, various solution-processed electron injection materials have been mainly employed in PLEDs because most π-conjugated polymers are insoluble in alcohol used as coating solvents of upper layer. It is difficult to fabricate multilayer structure with small molecule-based EML and solution-processed electron injection materials. Therefore, the combination of solution-processable EIL and small molecule EML are strongly desired.

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