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(54) **Title:** SOLUTION PROCESSED METAL ION COMPOUND DOPED ELECTRON TRANSPORT LAYERS AND USES IN ORGANIC ELECTRONICS

(57) **Abstract:** Compositions and methods for forming an electron transporting layer of an electronic device by solution processing, as well as electronic devices comprising solution-processed active layer and solution-processed electron transporting layer. The device can be an OLED. The composition comprises: (i) at least one electron transporting material having a molecular weight of 5,000 g/mol or less; (ii) at least one metal ion compound dopant of the electron transporting material; and (iii) at least one solvent capable of dissolving the electron transporting material and the dopant.



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**SOLUTION PROCESSED METAL ION COMPOUND DOPED ELECTRON
TRANSPORT LAYERS AND USES IN ORGANIC ELECTRONICS**

BACKGROUND

Organic electronic devices, including electroluminescence devices, photovoltaic devices, and field-effect transistors, are of tremendous commercial interest. Recently, intensive efforts have been focused on developing phosphorescent OLEDs (PhOLEDs), which utilize triplet excitons to achieve superior performance compare to conventional fluorescent OLEDs. Highly efficient multilayered PhOLEDs are generally fabricated by sequential deposition of multilayered structures that facilitate charge-injection and transport from both electrodes to the emission layer (EML). Most high-performance PhOLEDs have been achieved by vacuum-deposition of small molecules involving sequential thermal evaporation to obtain the multilayered structures. In contrast to the intensive efforts made on developing highly efficient multilayered PhOLEDs by thermal vacuum evaporation, reports on solution-processed PhOLEDs are relatively few. Although solution-processing has advantages of low-cost fabrication and/or large-area devices, challenges remain in sequential solution-processing of a multilayered device structure because the solvent used to deposit the subsequent layer can easily dissolve or disrupt the underlayer. One general approach to overcome this problem is to employ orthogonal solvent processing.

Despite the demonstration of multilayered device structures fabricated by orthogonal solution-processing, improving electron-injection and transport from the metal cathode is a major challenge in realization of all-solution-processed PhOLEDs with higher performance. Various n-type doping approaches and basic mechanisms have been proposed and studied to achieve an increased charge carrier concentration with high conductivity to realize high-performance OLEDs. N-type doping of the organic ETMs (electron transporting material) is known to be challenging due to the difficulty of finding suitable n-type dopants. Nevertheless, such thermal evaporation or co-evaporation based doping is mainly carried out under expensive high vacuum condition, especially in the case of alkali metal salts. Also, for co-evaporation based doping, the precise control of the co-deposition rate via complicated vacuum thermal evaporation process is highly challenging and economically undesirable.

Therefore, a need exists for methods for fabricating n-type doped electron transporting layers (ETLs) of organic electronic devices by solution processing.

SUMMARY

Embodiments described herein include, for example, compositions, devices, and methods for making and methods of using the compositions and devices.

For example, provided is a composition suitable for being deposited by solution processing to form an electron transporting layer of an electronic device, said composition comprising: (i) at least one electron transporting material having a molecular weight of 5,000 g/mol or less; (ii) at least one metal ion compound dopant of the electron transporting material; and (iii) one or more solvents capable of dissolving the electron transporting material and the dopant.

Another embodiment provides a composition suitable for being deposited by solution processing to form an electron transporting layer of an electronic device, said composition prepared by combination of: (i) at least one electron transporting material having a molecular weight of 5,000 g/mol or less; (ii) at least one metal ion compound dopant of the electron transporting material; and (iii) one or more solvents capable of dissolving the electron transporting material and the dopant.

In one embodiment, the electron transporting material has a molecular weight of 2,000 g/mol or less.

In one embodiment, the electron transporting material comprises at least one 5-membered or 6-membered conjugated ring comprising at least one nitrogen heteroatom. In a further embodiment, the nitrogen heteroatom is present in protonated form.

In one embodiment, the electron transporting material comprises at least one conjugated ring selected from pyrrole, pyrazole, imidazole, oxazole, oxadiazole, triazole, indole, iso-indole, pyridine, pyrimidine, pyrazine, triazine, tetrazine, quinoline, iso-quinoline, and phenanthroline.

In one embodiment, the electron transporting material is 1,3,5-tris(*m*-pyrid-3-yl-phenyl)benzene (TmPyPB), 1,3-bis(3,5-di(pyridine-3-yl)phenyl)benzene (BmPyPB), 1,3,5-(tris(4-pyridinquinolin-2-yl)benzene (TPyQB), 1,3,5-tris(4-phenylquinolin-2-yl)benzene (TQB), 1,3,5-tris(4-methylquinolin-2-yl)benzene (TMQB), 1,3,5-tris(4-(4-fluorophenyl)quinolin-2-yl)benzene (TFQB), 4,7-diphenyl-1,10-phenanthroline (BPhen), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), tris(2,4,6-trimethyl-3-(pyridine-3-yl)phenyl)borane (3TPyMB), 2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole (TPBI), 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD), 1,3-bis(2-(4-*tert*-

butylphenyl)-1,3,4-oxadiazol-5-yl)benzene (OXD-7), 2,4,6-tris(diphenylamino)-1,3,5-triazine (TRZ), or a combination thereof.

In one embodiment, the dopant is an alkali or alkaline earth metal ion compound represented by MX , M_2X , M_3X or MX_2 , M is Li, Na, K, Cs, Rb, Ca, Mg, Ba or Sr, and X is OH, F, Cl, Br, CO_3 , HCO_3 , C_2O_4 , SO_4 , PO_4 , BH_4 , CN or $RCOO$, R is hydrogen or a C_1 - C_3 optionally substituted alkyl or aryl. In one embodiment, the dopant is selected from Li_2CO_3 , Cs_2CO_3 , Li_2CO_3 , Cs_2CO_3 , Na_2CO_3 , K_2CO_3 , $Cs_2C_2O_4$, and $CsHCO_2$.

In one embodiment, the composition comprises a first polar solvent and a second polar solvent different from the first polar solvent. In another embodiment, the first polar solvent is water or a C_1 - C_3 alcohol, and the second polar solvent is C_1 - C_4 carboxylic acid optionally substituted with one or more fluorine. In a further embodiment, the first polar solvent is water, the second polar solvent is formic acid, and the molar ratio of water to formic acid is between 1:1 and 1:9.

In one embodiment, the weight of the dopant, based on the total weight of the electron transporting material and of the dopant, is between 0.1% and 20%.

Also provided is a method, comprising: (i) providing a composition described above; and (ii) depositing said composition by solution processing and drying to form an electron transporting layer of an electronic device.

In one embodiment, the electron transporting layer is formed under air and at a temperature lower than 100°C . In a further embodiment, the composition is deposited over an active layer of an electronic device, and the active layer is not solvated during the solution processing of the electron transporting layer.

Also provided is a method for manufacturing an electronic device, comprising (i) depositing an active layer of the electronic device by solution processing, then (ii) applying the method described above to form the electron transporting layer of the electronic device.

Further provided is an electronic device, comprising: (i) an active layer susceptible of being formed by solution processing; and (ii) an electron transporting layer obtained by any of the methods described above.

In one embodiment, the electronic device is an electroluminescence device, a photovoltaic device, or a field-effect transistor. In a further embodiment, the electronic device is an OLED device comprising at least one phosphorescent emitter dispersed in a host material having a molecular weight of 5,000 g/mol or less as the active layer, and the OLED device has an external quantum efficiency of at least 10% at $1,000\text{ cd/m}^2$.

Another embodiment is a composition prepared by: (A) combining: (i) at least one electron transporting material having a molecular weight of 5,000 g/mol or less; (ii) at least one metal ion compound dopant of the electron transporting material; and (iii) one or more solvents capable of dissolving the electron transporting material and the dopant; to form a first composition, and (B) forming a film from the first composition by removing solvent.

At least one advantage for one embodiment is high performance including efficiency and brightness, as well as good efficiency at high brightness. Other advantages for at least some embodiments include ability to control compositional quality and consistency. The advantages of solution processing, such as economic and large area processing, can be achieved for at least some embodiments.

In particular, for some embodiments, ETLs of OLEDs were fabricated by solution-processing from small-molecule electron-transport materials doped with alkali metal salts to achieve high-performance all-solution-processed PhOLEDs. It was found that incorporation of the dopant into the ETL by solution-processing significantly changes the surface morphology of ETL forming a good interfacial contact between ETL and metal cathode, which can be a factor leading to facile electron-injection and transport. These results show that solution-processing of metal salt doped small-molecule ETMs is a new strategy that enables the fabrication of various high-performance multilayered all-solution-processed organic electronic devices.

More particularly, for some embodiments, high performance solution-processed blue PhOLEDs were achieved by sequential solution-processing of electron-transport material doped with an alkali metal salt, cesium carbonate (Cs_2CO_3) or lithium carbonate (Li_2CO_3). PhOLEDs based on FIrpic blue triplet emitter-doped poly(*N*-vinylcarbazole) emission layer and a solution-processed 4,7-diphenyl-1,10-phenanthroline (Bathophenanthroline, BPhen) electron-transport layer (ETL) doped with Cs_2CO_3 show a luminous efficiency (LE) of 35.1 cd A^{-1} at a brightness of 1820 cd m^{-2} with a power efficiency of 15.0 lm W^{-1} and an external quantum efficiency of 17.9%. Furthermore, the approach of solution-processing of alkali metal salt doped ETL was readily extended to other small-molecule electron-transport materials, including 1,3,5-tris(4-pyridinquinolin-2-yl)benzene (TPyQB), 1,3,5-tris(*m*-pyrid-3-yl-phenyl)benzene (TmPyPB), and 1,3-bis(3,5-di(pyridine-3-yl)phenyl)benzene (BmPyPB). For example, the blue PhOLEDs with solution-processed BmPyPB ETL doped with Cs_2CO_3 show a high LE value of 37.7 cd A^{-1} at a brightness of 1300 cd m^{-2} with a power efficiency of

13.1 lm W⁻¹ and an external quantum efficiency of 19.0%, which is believed to be the highest (or close to highest) performance reported to date for all-solution-processed blue PhOLEDs.

Orthogonal solution-processing of metal salt-doped electron-transport materials is demonstrated to be an important strategy for applications in various solution-processed multilayered organic electronic devices.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows performance of exemplary blue PhOLEDs with BPhen ETL doped with Cs₂CO₃: (a) Current density (J) – voltage (V); (b) luminance (L) - voltage (V); (c) luminous efficiency (LE) - luminance (L); and (d) power efficiency (PE) - luminance (L) curves. Device structures: ITO/PEDOT:PSS(30 nm)/EML(70 nm)/solution-processed BPhen:Cs₂CO₃ ETL(20 nm)/Al (100 nm), ETL doped with different concentration of Cs₂CO₃; and ITO/PEDOT:PSS(30 nm)/EML(70 nm)/vacuum-deposited BPhen ETL(20 nm)/vacuum-deposited Cs₂CO₃(1 nm)/Al (100 nm).

Figure 2 shows performance of exemplary blue PhOLEDs with BPhen ETL doped with Li₂CO₃: (a) Current density (J) – voltage (V); (b) luminance (L) - voltage (V); (c) luminous efficiency (LE) - luminance (L); and (d) power efficiency (PE) - luminance (L) curves. Device structures: ITO/PEDOT:PSS(30 nm)/EML(70 nm)/solution-processed BPhen:Li₂CO₃ ETL(20 nm)/Al (100 nm), BPhen ETL doped with different concentration of Li₂CO₃; and ITO/PEDOT:PSS(30 nm)/EML(70 nm)/vacuum-deposited BPhen ETL(20 nm)/vacuum-deposited Li₂CO₃(1 nm)/Al (100 nm).

Figure 3 shows normalized EL spectra of exemplary blue PhOLEDs with: (a) BPhen:Cs₂CO₃; and (b) BPhen:Li₂CO₃ ETLs at the maximum brightness.

Figure 4 shows performance of exemplary blue PhOLEDs with TPyQB ETL doped with Cs₂CO₃: (a) Current density (J) – voltage (V); (b) luminance (L) - voltage (V); (c) luminous efficiency (LE) - luminance (L); and (d) power efficiency (PE) - luminance (L) curves. Device structures: ITO/PEDOT:PSS(30 nm)/EML(70 nm)/solution-processed TPyQB:Cs₂CO₃ ETL(20 nm)/Al (100 nm), TPyQB ETL doped with different concentration of Cs₂CO₃.

Figure 5 shows performance of exemplary blue PhOLEDs with TmPyPB ETL doped with Cs₂CO₃: (a) Current density (J) – voltage (V); (b) luminance (L) - voltage (V); (c) luminous efficiency (LE) - luminance (L); and (d) power efficiency (PE) - luminance (L) curves. Device structures: ITO/PEDOT:PSS(30 nm)/EML(70 nm)/solution-processed

TmPyPB:Cs₂CO₃ ETL(20 nm)/Al (100 nm), TmPyPB ETL doped with different concentration of Cs₂CO₃.

Figure 6 shows performance of exemplary blue PhOLEDs with BmPyPB ETL doped with Cs₂CO₃: (a) Current density (J) – voltage (V); (b) luminance (L) - voltage (V); (c) luminous efficiency (LE) - luminance (L); and (d) power efficiency (PE) - luminance (L) curves. Device structures: ITO/PEDOT:PSS(30 nm)/EML(70 nm)/solution-processed BmPyPB:Cs₂CO₃ ETL(20 nm)/Al (100 nm), BmPyPB ETL doped with different concentration of Cs₂CO₃.

Figure 7 shows AFM (atomic force microscope) topographical height images (left, 5 $\mu\text{m} \times 5 \mu\text{m}$) and the corresponding phase images (right, 5 $\mu\text{m} \times 5 \mu\text{m}$) of exemplary solution-processed BPhen ETL films doped with different concentration of Cs₂CO₃: (a) 0 wt%; (b) 5.0 wt%; (c) 7.5 wt%; (d) 10.0 wt%; (e) 12.5 wt%; and (f) 15.0 wt%.

Figure 8 shows AFM topographical height images (left, 5 $\mu\text{m} \times 5 \mu\text{m}$) and the corresponding phase images (right, 5 $\mu\text{m} \times 5 \mu\text{m}$) of exemplary solution-processed BPhen ETL films doped with different concentration of Li₂CO₃: (a) 0 wt%; (b) 1.0 wt%; (c) 2.5 wt%; (d) 5.0 wt%; (e) 7.5 wt%; and (f) 10.0 wt%.

Figure 9 shows performance of exemplary single charge-carrier dominant devices: (a) electron-dominant devices with solution-processed BPhen:Cs₂CO₃ ETLs; (b) electron-dominant devices with solution-processed BPhen:Li₂CO₃ ETLs; (c) hole-dominant devices with solution-processed BPhen:Cs₂CO₃ ETLs; and (d) hole-dominant devices with solution-processed BPhen:Li₂CO₃ ETLs. Device structures of electron-dominant devices: ITO/polymer host(70 nm)/solution-processed BPhen:Cs₂CO₃ ETL (20 nm)/Al; and hole-dominant devices: ITO/PEDOT:PSS(30 nm)/polymer host(70 nm)/ solution-processed BPhen:Li₂CO₃ ETL (20 nm)/Au.

Figure 10 shows current-voltage (I - V) characteristics of exemplary ITO/solution-processed BPhen:alkali metal salt dopant film (~200 nm)/Al devices in ambient conditions. (a) BPhen doped with different concentration of Cs₂CO₃; (b) BPhen doped with different concentration of Li₂CO₃.

Figure 11 shows (a) Luminance-voltage (L - V) and (b) luminous efficiency-luminance (LE - L) characteristics of exemplary blue PhOLEDs with solution-processed BPhen ETL. Device I: ITO/PEDOT:PSS/Blue EML/solution-processed BPhen/Al; Device II: ITO/PEDOT:PSS/Blue EML/solution-processed BPhen:Li₂CO₃/Al; Device III: ITO/PEDOT:PSS/Blue EML/solution-processed BPhen:Na₂CO₃/Al; Device IV:

ITO/PEDOT:PSS/Blue EML/solution-processed BPhen:K₂CO₃/Al; and Device V: ITO/PEDOT:PSS/Blue EML/solution-processed BPhen:Cs₂CO₃/Al.

Figure 12 shows (a) Luminance-voltage (L - V) and (b) luminous efficiency-luminance (LE - L) characteristics of exemplary blue PhOLEDs with solution-processed BPhen ETL. Device I: ITO/PEDOT:PSS/Blue EML/solution-processed BPhen/Al; Device II: ITO/PEDOT:PSS/Blue EML/solution-processed BPhen:Cs₂CO₃/Al; Device III: ITO/PEDOT:PSS/Blue EML/solution-processed BPhen:Cs₂(COO)₂/Al; and Device IV: ITO/PEDOT:PSS/Blue EML/solution-processed BPhen:CsHCO₂/Al.

DETAILED DESCRIPTION

INTRODUCTION

References cited herein are incorporated by reference in their entireties.

Provided herein are solution-deposited metal salt doped electron-transport layers (ETLs) and their uses to improve electron-injection and transport in organic light-emitting diodes (OLEDs) including phosphorescent OLEDs (PhOLEDs), and other electronic devices. By co-dissolving a metal salt with an electron-transport material in a solvent, the resulting solution can be deposited onto a device substrate by spin coating (or by other coating methods) and dried to create an ETL of precise composition, leading to enhanced overall performance of the PhOLED devices.

COMPOSITION FOR SOLUTION PROCESSING OF ELECTRON TRANSPORTING LAYER

Compositions described herein are suitable for making electron transporting layers by solution processing. The composition can comprise, for example, at least one electron transporting material, at least one dopant for the electron transporting material, and one or more solvents.

The composition can comprise, for example, at least two different electron transporting materials. The composition can comprise, for example, at least two different dopants. The composition can comprise, for example, at least two different solvents.

The composition can be, for example, a solution or dispersion adapted for solution processing including spin coating.

The solution or dispersion can be formed by, for example, adding at least one electron transporting material and at least one dopant into at least one solvent. The solution or dispersion can also be formed by, for example, mixing a first solution or dispersion comprising the electron transporting material and a second solution or dispersion comprising the dopant.

In one embodiment, the composition consists essentially of the at least one electron transporting material, the at least one dopant, and the one or more solvents. In another embodiment, the composition consists of the at least one electron transporting material, the at least one dopant, and the one or more solvents.

In one embodiment, the composition consists essentially of an electron transporting material, a dopant, and a binary solvent. In another embodiment, the composition consists of an electron transporting material, a dopant, and a binary solvent.

In some embodiment, a composition suitable for being deposited by solution processing to form an electron transporting layer of an electronic device, can be prepared by combining: (i) at least one electron transporting material having a molecular weight of 5,000 g/mol or less; (ii) at least one metal ion compound dopant of the electron transporting material; and (iii) one or more solvents capable of dissolving the electron transporting material and the dopant. The doping reaction, in different embodiments, can occur upon mixing and/or upon forming a film, including, for example, drying and heating.

The composition described herein can be, for example, solution deposited and dried to form an electron transporting layer. The subject matter of this application encompasses not only compositions comprising the mixture of the electron transporting material, the dopant and the solvent system before any doping or complexation reaction (the ingredients), but also compositions comprising the mixture of the electron transporting material, the dopant and the solvent system after any doping and/or complexation reaction. Further, the subject matter of this application also encompasses the electron transporting layer formed by solution processing and any other film-forming techniques such as drying, heating and solvent-removal. The doping or complexation reaction which occurs may not be fully understood but the inventions claimed herein are not limited by a complete understanding of any doping or complexation reaction which occurs upon mixing ingredients.

ELECTRON TRANSPORTING MATERIAL

Electron transporting materials are known in the art including as described in, for example, WO 2012/024132 and Duan *et al.*, *J. Mater. Chem.* 20:6392-6407 (2010), both of which are hereby incorporated by reference in their entireties.

The molecular weight of the electron transporting material can be, for example, 5,000 g/mol or less, or 3,000 g/mol or less, or 2,000 g/mol or less, or 1,000 g/mol or less. In one embodiment, the electron transporting material is a small molecule compound. In one embodiment, the electron transporting material is not a polymer. In one embodiment, the electron transporting material is not an oligomer.

The electron transporting material can comprise, for example, at least one, at least two, or at least three conjugated rings each comprising at least one heteroatom. The conjugated ring can be, for example, a five-membered ring or a six-membered ring. The conjugated ring can be, for example, part of a fused-ring system comprising two or more rings fused together.

The heteroatom in the conjugated ring can be, for example, N, O, S, Ge or Se. In one embodiment, the electron transporting material comprises at least one, at least two, or at least three conjugated rings each comprising at least one nitrogen. In another embodiment, the electron transporting material comprises at least one, at least two, or at least three imine nitrogens. The nitrogen can be, for example, present in its protonated form. In one embodiment, the nitrogen is in its protonated form in a composition comprising the electron transporting material, the dopant and the solvent system.

Examples of the conjugated ring described herein include pyrrole, pyrazole, imidazole, oxazole, oxadiazole, triazole, indole, iso-indole, pyridine, pyrimidine, pyrazine, triazine, tetrazine, quinoline, iso-quinoline, and phenanthroline.

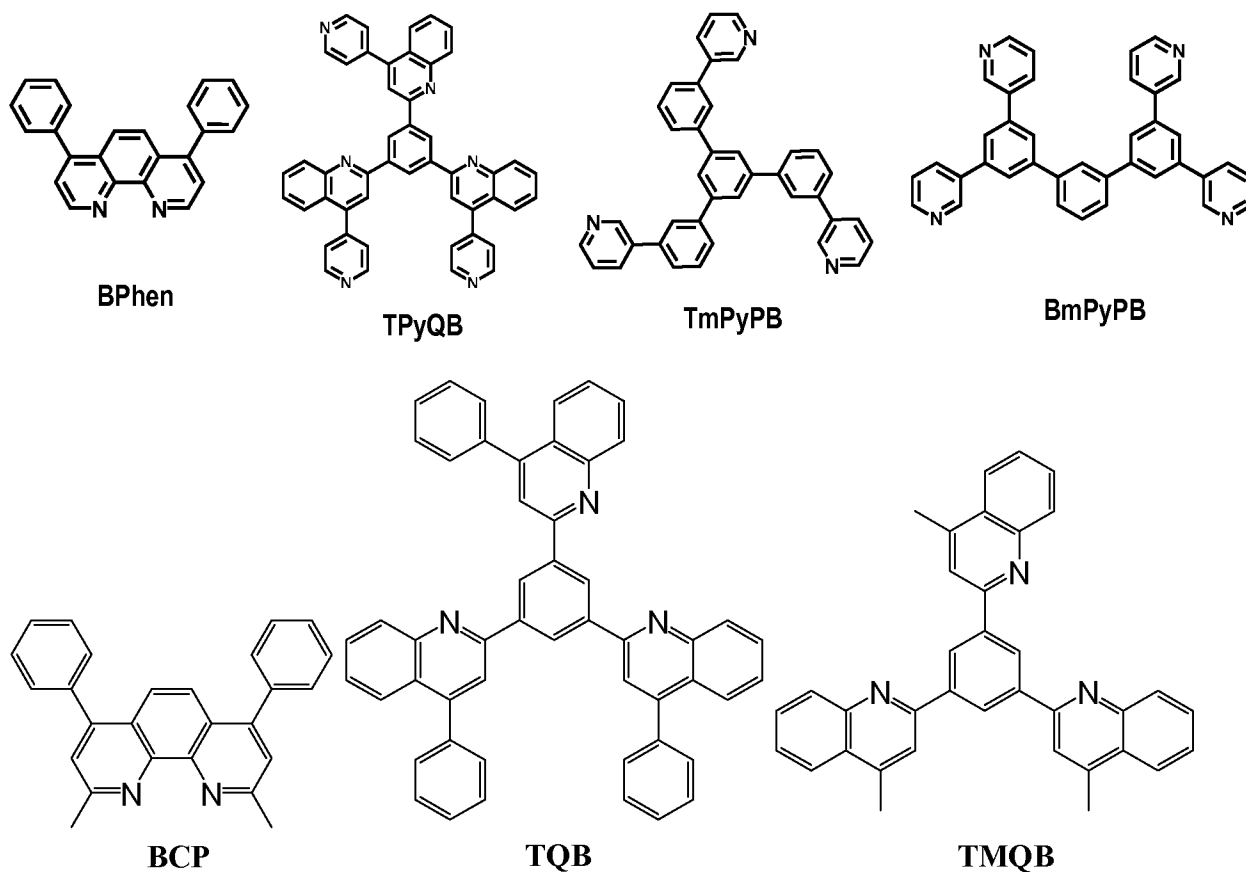
The electron transporting material can comprise, for example, at least one, at least two, or at least three optionally substituted pyridine rings. The electron transporting material can comprise, for example, at least one, at least two, or at least three optionally substituted quinoline rings.

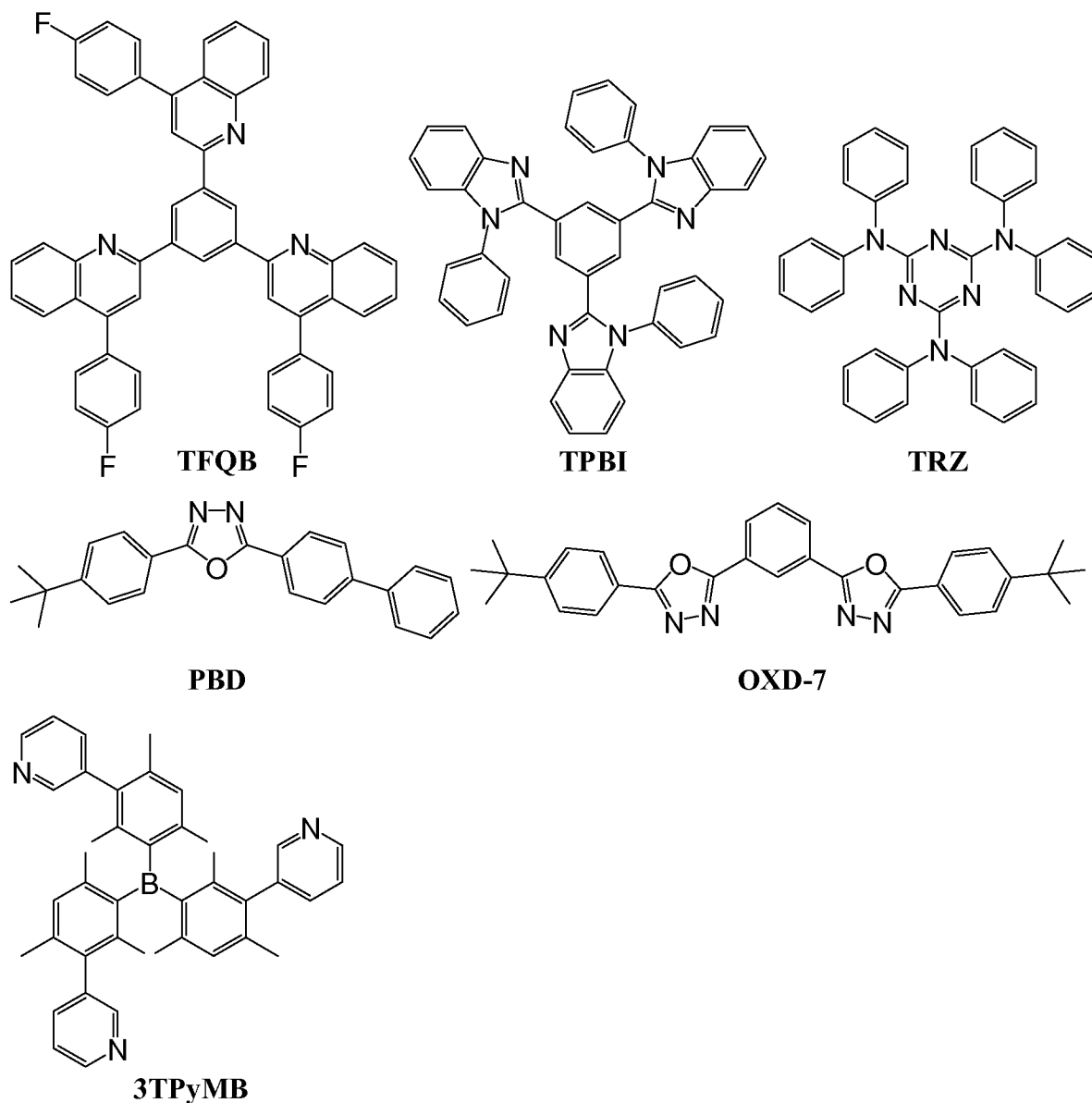
The electron transporting material can comprise, for example, at least one 1,3,5-trisubstituted benzene ring and at least three optionally substituted pyridine rings. The electron transporting material can comprise, for example, at least one 1,3,5-trisubstituted benzene ring and at least three optionally substituted quinoline rings.

The electron transporting material can comprise, for example, at least one optionally substituted phenanthroline group. The electron transporting material can comprise, for

example, at least one optionally substituted oxadiazole. The electron transporting material can comprise, for example, at least one optionally substituted triazole, triazine or tetrazine.

Examples of the electron transporting material described herein include 1,3,5-tris(*m*-pyrid-3-yl-phenyl)benzene (TmPyPB), 1,3-bis(3,5-di(pyridine-3-yl)phenyl)benzene (BmPyPB), 1,3,5-(tris(4-pyridinquinolin-2-yl)benzene (TPyQB), 1,3,5-tris(4-phenylquinolin-2-yl)benzene (TQB), 1,3,5-tris(4-methylquinolin-2-yl)benzene (TMQB), 1,3,5-tris(4-(4-fluorophenyl)quinolin-2-yl)benzene (TFQB), 4,7-diphenyl-1,10-phenanthroline (BPhen), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), tris(2,4,6-trimethyl-3-(pyridine-3-yl)phenyl)borane (3TPyMB), 2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole (TPBI), 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD), 1,3-bis(2-(4-*tert*-butylphenyl)-1,3,4-oxadiazole-5-yl)benzene (OXD-7), and 2,4,6-tris(diphenylamino)-1,3,5-triazine (TRZ).





In one embodiment, the electron transporting material does not comprise any ionic groups that can, at least in some cases, cause undesirable electrochemical doping effects and reduce the air stability of high work function electrodes.

DOPANTS

Dopants for electron transporting materials are known in the art and described in, for example, Werner *et al.*, *Appl. Phys. Lett.* **2003**, 82, 4495; Chan *et al.*, *Org. Electron.* **2008**, 9, 575; Cho *et al.*, *J. Mater. Chem.* **2011**, 21, 6956; Meyer *et al.*, *Appl. Phys. Lett.* **2010**, 96, 193302; Yook *et al.*, *Adv. Funct. Mater.* **2010**, 20, 1797; Ma *et al.*, *Adv. Funct. Mater.* **2010**, 20, 1371; and Walzer *et al.*, *Chem. Rev.* **2007**, 107, 1233, all of which are hereby incorporated by reference in their entireties.

The dopant can be, for example, a metal ion compound. The dopant can be, for example, an alkali metal ion compound. The dopant can be, for example, an alkaline earth metal ion compound.

The metal ion compound can be, for example, a metal salt. The metal ion compound can be, for example, an ionic compound comprising two ionic counterparts, a metal cation and an anion, including metal hydroxide and metal bicarbonate.

The dopant can be represented by, for example, MX, M₂X, M₃X or MX₂, wherein M is, for example, Li, Na, K, Cs, Rb, Ca, Mg, Ba or Sr, and wherein X is OH, F, Cl, Br, CO₃, HCO₃, C₂O₄, SO₄, PO₄, BH₄, CN or RCOO, wherein R is hydrogen or a C₁-C₃ optionally substituted alkyl or aryl. In one embodiment, the dopant is a Cs salt such as Cs₂CO₃, Cs₂C₂O₄, CsHCO₂ or CsF. In another embodiment, the dopant is a Li salt such as Li₂CO₃, Li₂C₂O₄, LiHCO₂ or LiF. In a further embodiment, the dopant is a Na salt such as Na₂CO₃, Na₂C₂O₄, NaHCO₂ or NaF. In an additional embodiment, the dopant is a K salt such as K₂CO₃, K₂C₂O₄, KHCO₂ or KF.

The weight percentage of the dopant, based on the total weight of the dopant and the electron transporting material, can be, for example, about 0.1% to about 20%, or about 1% to about 15%, or about 2.5% to about 12.5 %, or about 5% to about 10%. Another preferred range is 0.1% to 10%.

SOLVENT SYSTEM

The solvent system described herein are suitable for solution processing of the electron transporting material and the dopant therefor. Solvents for electron transporting materials are known in the art and described in, for example, WO 2012/024132 and Duan *et al.*, *J. Mater. Chem.* 20:6392-6407 (2010), incorporated by reference in their entireties.

The solvent system can comprise, for example, at least one solvent, or at least two solvents, or at least three solvents. The solvent system can comprise, for example, one or more polar protic solvents such as water, C₁-C₄ alcohol, and C₁-C₄ carboxylic acid optionally substituted with one or more halogens. The solvent system can comprise, for example, a volatile acid such as HCl.

The solvent system can comprise, for example, one or more polar aprotic solvents such as dimethyl sulfoxide, dimethylformamide, dioxane, tetrahydrofuran, and acetonitrile. The solvent system can comprise, for example, a mixture of multiple solvents that share ion capable of dissolving the electron transporting material and the dopant.

The solvent system can be, for example, a binary solvent system comprising a first polar solvent and a second polar solvent different from the first polar solvent. The first polar solvent and the second polar solvent can be suitable for respectively dissolving the dopant and the electron transporting material, such that their combination would be suitable for dissolving both the dopant and the electron transporting material in a single solution.

The first polar solvent can be, for example, water or a C₁-C₃ alcohol including methanol, ethanol, and propanol. The second polar solvent can be, for example, a C₁-C₄ carboxylic acid optionally substituted with one or more halogens such as F, including formic acid, acetic acid, 2-fluoro-acetic acid, 2-chloro-acetic acid, 2-propenoic acid, 2-propynoic acid, lactic acid, maleic acid, trifluoroacetic acid, trifluorobutanoic acid, trifluoropropionic acid, and perfluoropropanoic acid.

A list of exemplary carboxylic acids suitable for the solvent system described herein are provided below in a Table. The acids are selected based on boiling point (Bp ~ 70-160 °C) and pKa lower than 5.

Acid	Structure	b.p.	pKa
Formic acid	HCOOH	100	3.74
Acetic acid	CH₃COOH	118	4.79
2-X-acetic acid	CH₂XCOOH X= F, Cl	165-189	2.66-3.17
2-Propenoic acid	CH₂CHCOOH	141	4.25
2-Propynoic acid	CHCHCOOH	144	2.0
Lactic acid	CH₃CHOHCOOH	122	3.86
Maleic acid	HOOCCHCHCOOH	135	2.39
Trifluoroacetic acid	CF₃COOH	72	.05
Perfluoropropionic acid	CF₃CF₂COOH	96	0.38
Trifluorobutyric acid	CF₃CF₂CF₂COOH	120	0.37
Trifluoropropionic acid	CF₃CH₂COOH	144	3.16

In the binary solvent system, the molar ratio between the first polar solvent and the second polar solvent can be, for example, 19:1 to 1:19, or 9:1 to 1:9, or 1:1 to 1:9, or 1:1 to 1:7, or 1:1 to 1:5, or 1:2 to 1:5.

In a particular embodiment, the solvent system can comprise water and formic acid. The molar ratio between water and formic acid can be, for example, 1:1 to 1:9, or 1:1 to 1:7, or 1:1 to 1:5, or 1:2 to 1:5, or about 1:3. In another particular embodiment, the solvent system comprises water and trifluoroacetic acid. In a further particular embodiment, the solvent system comprises water and lactic acid.

SOLUTION-PROCESSING OF ELECTRON TRANSPORTING LAYER

Solution processing methods are known in the art and described in, for example, WO 2012/024132 and Duan *et al.*, *J. Mater. Chem.* 20:6392-6407 (2010), incorporated by reference in their entireties. For example, spin coating, drop coating, and any other solution-based deposition techniques can be used to deposit the composition comprising the electron transporting material and the dopant. Subsequently, the solvent can be removed by techniques such as drying to form the electron transporting layer.

The electron transporting layer can be, for example, solution-deposited over an active layer of an electronic device. In one embodiment, the electron transporting layer is solution-deposited over an emissive layer of an electroluminescence device such as an OLED device. In another embodiment, the electron transporting layer is solution-deposited over an active layer of an photovoltaic device such as an organic solar cell.

Following solution-deposition, the electron transporting layer can be formed, for example, under air and at a temperature of 150°C or less, or 120°C or less, or 100°C or less, or 80°C or less, or 50°C or less. Further, the electron transporting layer can be formed, for example, under vacuum and at a temperature of 150°C or less, or 120°C or less, or 100°C or less, or 80°C or less, or 50°C or less. A minimum temperature can be, for example 25°C, or 35°C, or 45°C

The electron transporting layer formed by solution processing can have a root-mean square surface roughness of, for example, at least 0.3 nm, or at least 0.4 nm, or at least 0.5 nm, or at least 0.6 nm, or at least 0.7 nm, or at least 0.8 nm, or at least 0.9 nm, or at least 1.0 nm.

The solvent system used for dissolving the electron transporting material and the dopant can be, for example, orthogonal to the solubility of the active layer of the electronic devices. Orthogonal solution processing is described in Kim *et al.*, *ACS Appl. Mater.*

Interfaces **2010**, 2, 2974; Sax *et al.*, *Adv. Mater.* **2010**, 22, 2087; Kim *et al.*, *Appl. Phys. Lett.* **2011**, 99, 173303; and Liu *et al.*, *Synth. Met.* **2011**, 161, 426, incorporated by reference in their entireties

In one embodiment, the electron transporting layer is solution-deposited over the active layer, wherein the active layer is not solvated during the solution processing of the electron transporting layer. In another embodiment, the active layer is solution-deposited over the solution-processed electron transporting layer (*i.e.*, inverted device structure), wherein the electron transporting layer is not solvated during the solution processing of the active layer.

In a particular embodiment, both the electron transporting layer and the active layer of the electronic device are fabricated by solution processing.

The reactions which can occur in solution or in the solid state are not fully understood. However, the claimed inventions are not limited by the scientific theory of this process of mixing ingredients. In one embodiment, the electron transport layer formed by solution processing comprises a complex of the electron transporting material and the metal ion compound. In one embodiment, the electron transport layer formed by solution processing comprises a complex of the electron transporting material and the metal. In one embodiment, the electron transport layer formed by solution processing comprises a complex of the electron transporting material, the metal and formate. In one embodiment, the electron transport layer formed by solution processing comprises a complex of the electron transporting material, the metal and carbonate.

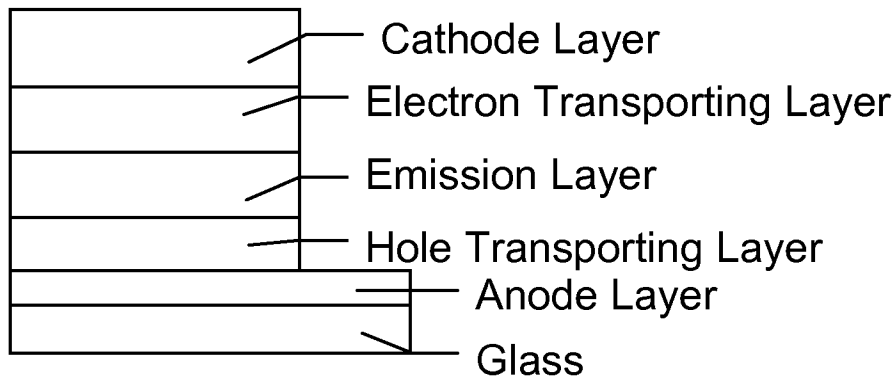
In one embodiment, the electron transport layer formed by solution processing comprises an electron transporting layer comprising at least one, at least two or at least three nitrogen heteroatoms in neutral form. In another embodiment, the electron transport layer formed by solution processing comprises an electron transporting layer comprising at least one, at least two or at least three nitrogen heteroatoms in protonated form. In one embodiment, the electron transport layer formed by solution processing comprises an electron transporting layer comprising at least one, at least two or at least three imine nitrogens in neutral form. In another embodiment, the electron transport layer formed by solution processing comprises an electron transporting layer comprising at least one, at least two or at least three imine nitrogens in protonated form.

ELECTRONIC DEVICES COMPRISING SOLUTION-PROCESSED ELECTRON TRANSPORTING LAYER

The solution-processed electron transporting layer described herein can be used in various electronic devices, including electroluminescence devices such as OLED devices, photovoltaic devices such as organic solar cells, as well as organic field-effect transistors.

In a particular embodiment, the electronic device comprising the solution-processed electron transporting layer is an OLED device.

Although other alternatives are known in the art, in many embodiments, the OLED devices comprise at least an anode layer, a hole transporting layer, an emission layer, an electron transporting layer, and a cathode layer. Such devices are illustrated in the diagram below.



The thickness of the anode layer, the cathode layer, the emissive layer, the hole transporting layer, and the electron transporting layer can be, for example, about 0.001-1000 μm , about 0.005-100 μm , or about 0.01-10 μm , or about 0.02-1 μm .

Many suitable materials for anode in electroluminescence devices are known in the art and include, for example, ITO, which can be applied, for example, as a vacuum-deposited layer over an inert and transparent substrate such as glass. Other examples include metal oxide with high work function, such as zinc oxide and indium zinc oxide.

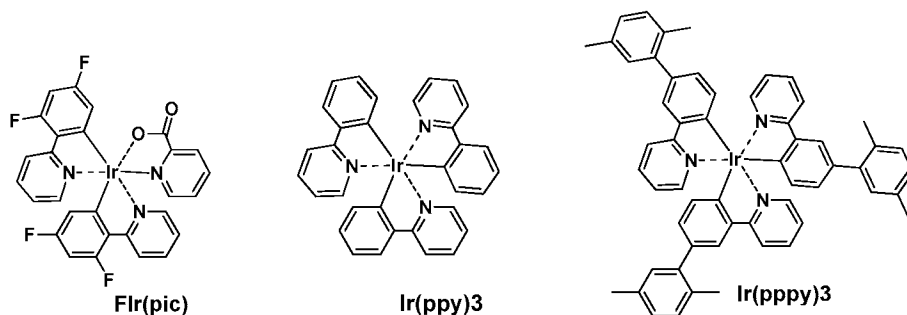
Many suitable materials for cathode in electroluminescence devices are known in the art and include, for example, Al and Ag, which can be applied, for example, as a vacuum-deposited layer over an electron transporting layer or an electron injection layer.

Many suitable materials for the hole transporting layer of electroluminescence devices are known in the art. Suitable hole transporting materials include, for example, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), hole transporting materials described in, for example, WO 2009/080799, which is incorporated herein by reference in its entirety, as well as other hole transporting materials known in the art. In one embodiment,

the hole transporting layer is fabricated by solution processing (e.g., spin coating) from a solution comprising the hole transporting material.

Many suitable materials for the emissive layer of electroluminescence devices are known in the art. Suitable host materials include, for example, polyvinylcarbazole (PVK), 4,4'-Bis(carbazol-9-yl)biphenyl (CBP), host materials described in WO 2010149618, WO 2010149620, WO 2010149622, PCT/US2011/063760 and PCT/US2011/066597, all of which are incorporated herein by reference in their entireties, as well as other host materials known in the art.

Suitable guest materials include, for example, Iridium complexes such as Bis(3,5-difluoro-2-(2-pyridyl)phenyl-(2-carboxypyridyl)iridium (III) (FIr(pic)), Tris(2-phenylpyridine)iridium(III) (Ir(ppy)₃) and Tris(5-phenyl-10,10-dimethyl-4-azatricycloundeca-2,4,6-triene)Iridium(III) (Ir(pppy)₃), guest materials described in WO 2011000873 and PCT/US2011/066597, both of which are incorporated herein by reference in their entirety, as well as other guest materials known in the art. The guest material can comprise at least one blue emitter, at least one green emitter, and/or at least one red emitter.



In one embodiment, the emissive layer is fabricated by solution processing (e.g., spin coating) from a solution comprising the host material and the guest material.

In one embodiment, the hole transporting layer, the emissive layer and the electron transporting layer described herein are all fabricated by solution processing, in particular orthogonal solution processing.

In some embodiments, the electroluminescence device comprises a solution-processed electron transporting layer described herein and an emissive layer comprising a blue emitter such as FIr(pic). The external quantum efficiency of said electroluminescence device at 1,000 cd/m² can be, for example, at least 5%, or at least 10%, or at least 15%, or at least 20%.

In some embodiments, the electroluminescence device comprises a solution-processed electron transporting layer described herein and a solution-processed emissive layer comprising a blue emitter such as FIr(pic). The external quantum efficiency of said

electroluminescence device at 1,000 cd/m² can be, for example, at least 5%, or at least 10%, or at least 15%, or at least 20%.

In some embodiments, the electroluminescence device comprises a solution-processed electron transporting layer described herein, a solution-processed hole transporting layer, and a solution-processed emissive layer comprising a blue emitter such as FIrpic). The external quantum efficiency of said electroluminescence device at 1,000 cd/m² can be, for example, at least 5%, or at least 10%, or at least 15%, or at least 20%.

WORKING EXAMPLES

Example 1 - Materials

Poly(*N*-vinyl carbazole) (PVK, average $M_w = 1,100,000 \text{ g mol}^{-1}$), 4,7-diphenyl-1,10-phenanthroline (BPhen, 99%, sublimed grade), cesium carbonate (Cs₂CO₃, 99.9% trace metals basis), and lithium carbonate (Li₂CO₃, 99%) were purchased from Sigma-Aldrich Co. 1,3-Bis(2-(4-*tert*-butylphenyl)-1,3,4-oxadiazole-5-yl)benzene (OXD-7), bis(3,5-difluoro-2-(2-pyridyl)phenyl)-(2-carboxypyridyl)iridium(III) (FIrpic), 1,3,5-Tris(*m*-pyrid-3-yl-phenyl)benzene (TmPyPB), and 1,3-bis(3,5-di(pyridine-3-yl)phenyl)benzene (BmPyPB) were purchased from Luminescence Technology (LumTec) Co., Taiwan. 1,3,5-tris(4-pyridinquinolin-2-yl)benzene (TPyQB) was synthesized according to WO 2012/024132, incorporated by referenced in its entirety. A solution of PEDOT:PSS (poly-(ethylenedioxythiophene):polystyrenesulfonate, Clevios P VP CH 8000) dispersed in water was purchased from Heraeus GmbH, Germany. All purchased chemicals were used as received without further purification.

Example 2 – Device Fabrication

The phosphorescent emission layer (EML) consisted of a blend of PVK and OXD-7 (PVK:OXD-7 = 60:40, wt/wt) as a host and 10.0 wt% FIrpic as the blue dopant. A solution of PEDOT:PSS was diluted with DI water by 1:1 ratio and filtered before spin-coating to make a 30-nm hole-injection layer onto a pre-cleaned ITO glass. Clevios P VP CH 8000 (PEDOT:PSS) was used to prevent current leakage and suppressing of hole-current. The film was then annealed at 150 °C under vacuum to remove residual water. The 70-nm polymer EML was obtained by spin coating of the PVK:OXD-7:FIrpic blend in chlorobenzene onto the PEDOT:PSS layer and vacuum dried at 100 °C. A small-molecule electron-transport

material (ETM, e.g. BPhen) was co-dissolved with alkali metal salt (Cs_2CO_3 or Li_2CO_3) in formic acid:water ($\text{FA}:\text{H}_2\text{O} = 3:1$) mixture and spun cast onto the EML at a spin speed of 7000 rpm followed by vacuum drying at 50 °C to form an electron-transport layer (ETL). After drying, thermally evaporated Al cathode was deposited onto the ETL. The structure of PhOLEDs with solution-processed ETLs was: ITO/PEDOT:PSS(30 nm)/EML(70 nm)/solution-processed ETM:alkali metal salt (20 nm)/Al (100 nm). The device structure of PhOLEDs with a vacuum-deposited bilayer of BPhen ETL and alkali metal salt was: ITO/PEDOT:PSS(30 nm)/EML(70 nm)/vacuum-deposited BPhen ETL (20 nm)/vacuum-deposited Cs_2CO_3 or Li_2CO_3 (1 nm)/Al. BPhen and alkali metal salt were sequentially vacuum-deposited by thermal evaporation onto EML using Edwards Auto Vacuum 306, followed by a deposition of Al without breaking the vacuum ($< 2.0 \times 10^{-6}$ torr).

For the single charge carrier-dominant devices, two types of devices were fabricated. Electron-dominant devices: ITO/polymer host (70 nm)/solution-deposited BPhen: M_2CO_3 ETL (20nm)/Al; and hole-dominant devices: ITO/PEDOT:PSS (30 nm)/polymer host (70 nm)/solution-deposited BPhen: M_2CO_3 ETL (20 nm)/Au. All layers were deposited under exactly the same conditions as the fabrication of PhOLEDs.

Devices for space-charge-limited current (SCLC) measurement were fabricated with ITO/solution-processed BPhen: M_2CO_3 ETL (~ 200 nm)/Al structure. The organic layer was obtained by the spin-coating of ETM solution onto the substrate followed by deposition of Al electrode.

Example 3 – Characterization

Film thickness was measured by an Alpha-Step 500 profilometer (KLA-Tencor, San Jose, CA) and also confirmed by Atomic Force Microscopy (AFM). Electroluminescence (EL) spectra were obtained using the same spectrofluorimeter described above. Current-voltage (J - V) characteristics of the PhOLEDs were measured by using a HP4155A semiconductor parameter analyzer (Yokogawa Hewlett-Packard, Tokyo). The luminance (brightness) was simultaneously measured by using a model 370 optometer (UDT Instruments, Baltimore, MD) equipped with a calibrated luminance sensor head (Model 211) and a 5x objective lens. The device external quantum efficiencies (EQEs) were calculated from the forward viewing luminance, current density and EL spectrum assuming a Lambertian distribution using procedures reported previously. All the device fabrication and device characterization steps were carried out under ambient laboratory condition.

Current-voltage characteristics of single charge carrier dominant and SCLC devices were measured using the same semiconductor parameter analyzer as used for PhOLED devices. The measurements were performed under dark and ambient conditions. AFM characterization of surface morphology was done on a Veeco Dimension 3100 Scanning Probe Microscope (SPM) system. The AFM topographical images were directly measured on the same PhOLEDs used for device characterization.

Example 4 – Performance of PhOLEDs with alkali metal salt doped BPhen ETLs

Solution-processed multilayered PhOLEDs with polymer-based blue phosphorescent emission layer (EML) and solution-deposited BPhen electron-transport layer (ETL) doped with an alkali metal salt (M_2CO_3 , $M = Li, Cs$) dopant, Cs_2CO_3 or Li_2CO_3 , were fabricated as discussed above. The concentration of the dopant in the ETL was: 2.5, 5.0, 7.5, 10.0, 12.5 or 15.0 wt% Cs_2CO_3 and 1.0, 2.5, 5.0, 7.5 or 10.0 wt% Li_2CO_3 . The blend of BPhen and alkali metal salt, BPhen: Cs_2CO_3 or BPhen: Li_2CO_3 ETL, was deposited from a formic acid (FA) / water (H_2O) solvent mixture (FA: $H_2O = 3:1$) onto the EML. A series of PhOLEDs with solution-processed BPhen: M_2CO_3 ETL were fabricated:

ITO/PEDOT:PSS/EML/BPhen: M_2CO_3 /Al; the metal salt (M_2CO_3 , $M = Cs, Li$) concentration was varied in the ETL. To verify the relative effectiveness of the solution-processed BPhen: M_2CO_3 -doped ETLs, PhOLEDs with a vacuum-deposited BPhen ETL and an alkali metal salt electron-injection layer (EIL) were also fabricated:

ITO/PEDOT:PSS/EML/vacuum-deposited BPhen/vacuum-deposited Cs_2CO_3 or Li_2CO_3 /Al.

Figure 1 shows the performance of PhOLEDs with solution-processed BPhen: Cs_2CO_3 ETL. As shown in **Figure 1a-1d**, the PhOLEDs with solution-deposited BPhen ETL without Cs_2CO_3 dopant (BPhen: Cs_2CO_3 0 wt%) showed a high turn-on voltage of 7.7 V, a drive voltage of 16.4 V and lower current density compared to other devices with BPhen ETL doped with Cs_2CO_3 . The performance of the PhOLEDs dramatically changes when Cs_2CO_3 is incorporated into BPhen ETL (**Figure 1, Table 1**). PhOLEDs with 2.5 wt% Cs_2CO_3 dopant showed a significantly reduced turn-on voltage (4.8 V), drive voltage (13.9 V), and also a significantly increased luminous efficiency (LE) of 26.4 cd A^{-1} with a power efficiency (PE) of 8.5 lm W^{-1} (external quantum efficiency (EQE) = 13.5 %). This represents a 1.6-fold higher efficiency compared to the device without Cs_2CO_3 dopant. As the concentration of Cs_2CO_3 in BPhen ETL increased from 2.5 to 10.0 wt%, the PhOLEDs showed much enhanced performance; the current density and maximum luminance

(brightness) increased while the turn-on voltage and drive voltage decreased (**Figure 1a, 1b, Table 1**). The blue PhOLEDs with solution-processed BPhen:Cs₂CO₃ (10.0 wt% Cs₂CO₃) showed the highest luminous efficiency (LE) of 35.1 cd A⁻¹ (at 1820 cd m⁻²) (**Figure 1c**) and the maximum power efficiency (PE) of 15.0 lm W⁻¹ (**Figure 1d**) with an EQE of 17.9 %, which is more than two-fold superior compared to the devices without Cs₂CO₃ doping. Even compared to the devices with vacuum-deposited BPhen ETL and Cs₂CO₃ EIL layers, PhOLEDs with solution-processed BPhen ETL doped with Cs₂CO₃ showed much superior performance. It is noted that PhOLEDs with solution-processed ETL reached the maximum efficiency at high brightness (1820 - 3600 cd m⁻²) while the devices with vacuum-deposited ETL/EIL showed the maximum efficiency at low brightness of 320 cd m⁻². Furthermore, PhOLEDs with vacuum-deposited ETL/EIL showed severe efficiency roll-off (**Figure 1c, 1d**) in contrast to the devices with solution-processed doped ETLs. These results suggest that the solution-processing of metal salt doped small-molecule electron-transport layer is promising for achieving high efficiency devices with high brightness.

A further increase of the Cs₂CO₃ concentration in BPhen:Cs₂CO₃ ETL to 12.5 and 15.0 wt% resulted in decreased device performance, even though these later PhOLEDs have similar current density (*J-V*) characteristics as the devices with 10.0 wt% Cs₂CO₃ (**Figure 1a**). PhOLEDs with 12.5 and 15.0 wt% Cs₂CO₃ -doped ETLs showed a higher turn-on and drive voltages and lower device efficiencies compared to the devices with 10.0 wt% Cs₂CO₃ (**Figure 1b-1d, Table 1**). These later PhOLEDs (> 10% Cs₂CO₃ ETLs) also showed efficiency roll-off as the brightness increases.

The *J-V*, *L-V*, *LE-L*, and the *PE-L* characteristics of PhOLEDs with BPhen ETLs doped with Li₂CO₃ are shown in **Figure 2**. Incorporation of Li₂CO₃ in the solution-processed BPhen ETL show significantly improved device performance. PhOLED with 1.0 wt% of Li₂CO₃ showed an increased LE value of 19.8 cd A⁻¹ (at 4030 cd m⁻²) and a PE value of 5.7 lm W⁻¹ (EQE of 10.1 %) compared to the device without Li₂CO₃ doping. As the Li₂CO₃ concentration increased to 2.5 and 5.0 wt%, the PhOLEDs showed much more enhanced performance. PhOLEDs with solution-deposited BPhen ETL doped with 2.5 wt% Li₂CO₃ gave a LE value of 27.1 cd A⁻¹ and a PE value of 10.4 lm W⁻¹ (EQE of 13.8%), while the PhOLEDs with 5.0 wt% Li₂CO₃ showed the highest device performance with an LE value of 27.9 cd A⁻¹ and EQE of 14.2 % (PE = 10.1 lm W⁻¹) with significantly reduced turn-on voltage of 4.4 V and a drive voltage of 12.3 V compared to the devices without Li₂CO₃ dopant (**Figure 2c, 2d, Table 2**). However, a further increase of the Li₂CO₃ concentration to 7.5 and 10.0 wt% resulted in a decreased device performance with LE values of 26.0 and 20.7 cd A⁻¹

(PE values of 9.2 and 8.0 lm W⁻¹), respectively, even though the *J-V* characteristics of these later devices were similar compared to the devices with 5.0 wt% Li₂CO₃-doped ETL (**Figure 2a**).

Similar to the PhOLEDs with BPhen:Cs₂CO₃ ETLs, PhOLEDs with solution-processed BPhen ETL doped with 2.5 - 5.0 wt% Li₂CO₃ had superior performances compared to the devices with vacuum-deposited BPhen ETL/Li₂CO₃ EIL. It is also noted that PhOLEDs with vacuum-deposited ETL/EIL showed the maximum LE value (23.0 cd A⁻¹) and PE value (11.8 lm W⁻¹) at low brightness (~ 120 cd m⁻²), whereas the devices with solution-processed ETL doped with Li₂CO₃ showed the highest efficiency at high brightness (1720 - 4340 cd m⁻²). These results clearly demonstrate that the solution-processing of ETL doped with alkali metal salt is a promising strategy to achieve high-performance blue PhOLEDs with high brightness. The device characteristics of the blue PhOLEDs with solution-processed BPhen ETL are summarized in **Table 1 and 2**.

The electroluminescence (EL) spectra of all the blue PhOLEDs, including those containing BPhen:Cs₂CO₃ or BPhen:Li₂CO₃ ETLs, are identical in lineshape with a maximum peak at 472 nm, which originates from the FIrpic blue triplet emitter (**Figure 3**). The Commission Internationale de L'Eclairage (CIE) 1931 coordinates of the devices were identical at (0.14, 0.28). It was observed that there is a slight increase of the vibronic shoulder around 500 nm in the case of PhOLEDs with solution-processed BPhen ETLs doped with 7.5 wt% Cs₂CO₃ and 5.0 wt% Li₂CO₃, which can be due to microcavity effects.

An optical microcavity is a structure formed by reflecting faces on the two sides of a spacer layer or optical medium. The multiple internal reflections inside the emission layer of OLEDs can induce, at some specific wavelengths and layer thicknesses, a resonance of the light intensity (irradiance) distribution inside the OLED. The phenomenon described here as "microcavity effect" refers to enhancement of the emitted irradiance related to the position of the charge recombination zone moved to the bulk side of the emission layer by improved electron transport.

Table 1. Device characteristics of solution-processes PhOLEDs with BPhen ETL doped with Cs₂CO₃. [a]

ETL[b]	Dopant concentration [wt%]	V _{on} [d] [V]	Drive voltage [V]	Current density [mA cm ⁻²]	Luminance [cd m ⁻²]	Device efficiency [cd A ⁻¹ , lm W ⁻¹ , (%EQE)]
BPhen	0.0	7.7	16.4 <i>12.6</i>	133.4 <i>11.5</i>	11200 <i>1890</i>	8.4, 1.6, (4.3) <i>16.5, 4.1, (8.4)</i>
BPhen: Cs ₂ CO ₃	2.5	4.8	13.9 <i>10.2</i>	108.9 <i>13.6</i>	14800 <i>3600</i>	13.6, 3.0, (6.9) <i>26.4, 8.5, (13.5)</i>
BPhen: Cs ₂ CO ₃	5.0	4.8	13.2 <i>8.9</i>	107.5 <i>9.0</i>	14600 <i>2530</i>	13.6, 3.2, (6.9) <i>28.1, 10.5, (14.3)</i>
BPhen: Cs ₂ CO ₃	7.5	4.6	12.8 <i>8.7</i>	103.3 <i>10.2</i>	18200 <i>3520</i>	17.6, 4.3, (8.9) <i>34.7, 13.1, (17.7)</i>
BPhen: Cs ₂ CO ₃	10.0	4.5	12.6 <i>7.8</i>	144.3 <i>5.2</i>	20100 <i>1820</i>	13.9, 3.4, (7.0) <i>35.1, 15.0, (17.9)</i>
BPhen: Cs ₂ CO ₃	12.5	4.8	12.4 <i>7.5</i>	177.5 <i>6.0</i>	17700 <i>1360</i>	9.6, 2.5, (4.9) <i>22.9, 9.6, (11.7)</i>
BPhen: Cs ₂ CO ₃	15.0	4.9	13.6 <i>7.6</i>	187.8 <i>4.2</i>	15100 <i>830</i>	8.0, 1.9, (4.0) <i>19.6, 8.1, (10.0)</i>
BPhen / Cs ₂ CO ₃ [c]	-	5.5	15.1 <i>7.6</i>	112.6 <i>1.2</i>	13400 <i>320</i>	11.9, 2.5, (6.1) <i>26.9, 11.7, (13.7)</i>

[a] Values in italic correspond to those at maximum device efficiencies. [b] PhOLEDs with solution-deposited BPhen ETL doped with Cs₂CO₃ or with vacuum-deposited BPhen/Cs₂CO₃ ETL/EIL. Device structures: ITO/PEDOT:PSS/EML/ETL/Al with solution-deposited doped BPhen ETL; and [c] ITO/PEDOT:PSS/EML/BPhen/Cs₂CO₃/Al with vacuum-deposited BPhen and Cs₂CO₃. [d] Turn-on voltage (at brightness of 1 cd m⁻²).

Table 2. Device characteristics of solution-processed PhOLEDs with BPhen ETL doped with Li₂CO₃. [a]

ETL[b]	Dopant concentration [wt%]	V _{on} [d] [V]	Drive voltage [V]	Current density [mA cm ⁻²]	Luminance [cd m ⁻²]	Device efficiency [cd A ⁻¹ , lm W ⁻¹ , (%EQE)]
BPhen	0.0	7.7	16.4 <i>12.6</i>	133.4 <i>11.5</i>	11200 <i>1890</i>	8.4, 1.6, (4.3) <i>16.5, 4.1, (8.4)</i>
BPhen: Li ₂ CO ₃	1.0	5.5	14.8 <i>11.4</i>	148.4 <i>20.4</i>	15700 <i>4030</i>	10.6, 2.5, (5.4) <i>19.8, 5.7, (10.1)</i>
BPhen: Li ₂ CO ₃	2.5	5.4	13.8 <i>9.1</i>	162.9 <i>6.4</i>	17800 <i>1720</i>	11.0, 2.5, (5.6) <i>27.1, 10.4, (13.8)</i>
BPhen: Li ₂ CO ₃	5.0	4.4	12.3 <i>8.9</i>	100.8 <i>12.8</i>	14500 <i>3600</i>	14.5, 3.7, (7.4) <i>27.9, 10.1, (14.2)</i>
BPhen: Li ₂ CO ₃	7.5	4.5	12.5 <i>9.2</i>	120.0 <i>16.7</i>	15600 <i>4340</i>	13.0, 3.3, (6.6) <i>26.0, 9.2, (13.2)</i>
BPhen: Li ₂ CO ₃	10.0	4.6	12.5 <i>8.4</i>	162.2 <i>11.7</i>	15800 <i>2430</i>	9.8, 2.5, (5.0) <i>20.7, 8.0, (10.6)</i>
BPhen / Li ₂ CO ₃ [c]	-	4.6	14.7 <i>6.5</i>	163.9 <i>0.52</i>	13400 <i>120</i>	8.1, 1.7, (4.1) <i>23.0, 11.7, (11.7)</i>

[a] Values in italic correspond to those at maximum device efficiencies. [b] PhOLEDs with solution-deposited BPhen ETL doped with Li₂CO₃ or with vacuum-deposited BPhen/Li₂CO₃ ETL. Device structures: ITO/PEDOT:PSS/EML/ETL/Al with solution-deposited doped BPhen ETL; and [c] ITO/PEDOT:PSS/EML/BPhen/Li₂CO₃/Al with vacuum-deposited BPhen and Li₂CO₃. [d] Turn-on voltage (at brightness of 1 cd m⁻²).

Example 5 – PhOLEDs with Cs₂CO₃ doped TPyQB/TmPyPB/BmPyPB ETLs

To further test the approach of solution-processing of alkali metal salt doped electron transport materials, various other known electron transport materials were investigated, including 1,3,5-tris(4-pyridinquinolin-2-yl)benzene (TPyQB), 1,3,5-tris(*m*-pyrid-3-yl-phenyl)benzene (TmPyPB), and 1,3-bis(3,5-di(pyridine-3-yl)phenyl)benzene (BmPyPB). The solution-processed ETL was doped with 5.0, 7.5, or 12.5 wt% Cs₂CO₃ and incorporated into multilayered blue PhOLEDs similar to BPhen:Cs₂CO₃ ETL devices described above.

PhOLEDs using solution-processed TPyQB ETL doped with Cs₂CO₃ were fabricated. (**Figure 4**). PhOLEDs with solution-processed TPyQB ETL without Cs₂CO₃ doping showed a turn-on voltage of 5.5 V, a drive voltage of 13.7 V and a lower current density compared to devices with TPyQB ETL doped with Cs₂CO₃. The performance of the PhOLEDs increased dramatically after incorporating Cs₂CO₃ into the TPyQB ETL. PhOLEDs with 7.5 wt% Cs₂CO₃-doped TPyQB ETL showed the highest performance with a reduced turn-on voltage (4.4 V), drive voltage (12.8 V), and a significantly increased LE value of 33.6 cd A⁻¹ with a PE value of 8.2 lm W⁻¹ (EQE = 17.1 %). Clearly, PhOLEDs with Cs₂CO₃-doped TPyQB ETL have far superior performance than those without Cs₂CO₃ doping. (**Figure 4c, 4d**)

Electron-transport materials with pyridyl groups were known as high triplet energy ETMs. For example, TmPyPB has a high triplet energy of 2.78 eV and a high electron mobility of $\mu_e = 1.0 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. As shown in **Figure 5**, the PhOLEDs with undoped TmPyPB had a much lower performance (LE = 16.5 cd A⁻¹, PE = 4.7 lm W⁻¹, and EQE = 8.4 %), whereas Cs₂CO₃-doped TmPyPB ETL led to a large enhancement of device performance. As shown in **Figure 5**, the performance of PhOLEDs with TmPyPB:Cs₂CO₃ (7.5 wt%) ETL showed a LE value of 37.7 cd A⁻¹ (PE = 14.1 lm W⁻¹, EQE = 19.0 %), which is the highest performance reported to date for all-solution-processed blue PhOLEDs.

PhOLEDs with solution-processed BmPyPB:Cs₂CO₃ ETLs were also fabricated. And, as expected, the PhOLEDs with BmPyPB ETL doped with Cs₂CO₃ similarly had a large enhancement in performance compared to non-doped ETL devices. The devices with BmPyPB ETL doped with 7.5 wt% Cs₂CO₃ showed an LE value of 37.4 cd A⁻¹ at a high brightness of 1760 cd m⁻², and a PE value of 16.1 lm W⁻¹ (with an EQE of 19.0 %, **Figure 6**). The performance of blue PhOLEDs incorporating BmPyPB:Cs₂CO₃ ETL at the doping concentration of 7.5 wt% Cs₂CO₃ is essentially identical with that of devices incorporating TmPyPB:Cs₂CO₃ at the same doping concentration. Further increase of the Cs₂CO₃ concentration in the TmPyPB:Cs₂CO₃ and BmPyPB:Cs₂CO₃ ETLs resulted in decreased

performance of the PhOLEDs (**Figures 5 and 6**) and these trends are very similar to those of PhOLEDs incorporating BPhen:Cs₂CO₃ ETLs.

These results demonstrate that the solution-processing of ETL doped with alkali metal salt is applicable to various small-molecule electron-transport materials of current interest for the fabrication of all-solution-processed multilayered OLEDs and other organic electronic devices. In particular, blue PhOLEDs with solution-processed TmPyPB:Cs₂CO₃ ETLs and BmPyPB:Cs₂CO₃ ETLs have the unexpectedly great performance.

Example 6 – Surface morphology of doped BPhen ETLs

The surface morphology of solution-deposited alkali metal salt-doped ETLs was investigated by atomic force microscopy (AFM). **Figure 7** shows AFM topographical height and the corresponding phase images of solution-deposited BPhen ETLs with different concentrations of Cs₂CO₃. BPhen ETL without Cs₂CO₃ doping has a smooth surface with root-mean-square (RMS) roughness of 0.312 nm (**Figure 7a**) whereas the solution-deposited Cs₂CO₃-doped BPhen ETLs show a significant change in surface morphology as the Cs₂CO₃ concentration increases (**Figure 7b-7f**). BPhen ETLs with 5.0 and 7.5 wt% Cs₂CO₃ have rougher surfaces (RMS values = 0.570 and 0.840 nm) compared to the BPhen ETL without Cs₂CO₃ doping (**Figure 7b, 7c**). As the Cs₂CO₃ concentration increases to 10.0 wt%, the ETL surface morphology becomes even much rougher, having an RMS roughness value of 1.12 nm (**Figure 7d**). In the light of the surface morphology variation with Cs₂CO₃ concentration in the ETL, while the present inventions are not limited by theory, it is suggested that in addition to n-doping effects of the alkali metal salt, the surface roughness of the solution-processed ETL, which enhances the ETL/Al contact area and thus facilitates efficient electron-injection. The rough surface morphology and vertical nanopillars formed in the solution-processed ETL leads to enhanced charge transport in the vertical direction and also provide good contact between ETL and Al cathode for facile electron-injection.

On the other hand, BPhen ETLs with a high Cs₂CO₃ concentration of 12.5 and 15.0 wt% have extremely rough surfaces with RMS roughness values of 2.53 and 5.53 nm (**Figure 7e and 7f**). At these high concentrations, phase separation in the BPhen:Cs₂CO₃ blend appears to occur and explains the observed decrease in device performance at high (> 10.0 wt%) Cs₂CO₃ concentrations. A significantly decreased charge-injection from cathode and charge-transport in the ETL can be expected when a separate insulating Cs₂CO₃ phase emerges in the ETL.

A similar trend was observed in the solution-processed BPhen ETLs doped with Li_2CO_3 . A smooth surface was observed in the AFM images of the solution-deposited BPhen ETL without the dopant (RMS value = 0.312 nm, **Figure 8a**) and the BPhen ETL doped with 1.0 wt% Li_2CO_3 (RMS value = 0.331 nm, **Figure 8b**), whereas BPhen ETLs doped with 2.5 (**Figure 8c**) and 5.0 wt% (**Figure 8d**) showed increased surface roughness with RMS values of 0.477 and 0.581 nm, respectively. The increased surface roughness is consistent with the improved performance of PhOLEDs with ETLs at these doping levels. On the other hand, solution-processed BPhen ETL at a higher concentration (10.0 wt% Li_2CO_3) showed phase-separated surface morphology (**Figure 8f**). The decreased performance of devices with BPhen ETLs doped at 10.0 wt% Li_2CO_3 is likely a consequence of such a phase-separated surface morphology. The observed surface morphology variation with alkali metal salt concentration in the doped ETL correlates very well with a similar observed variation of device performance with concentration of the alkali metal salt.

Example 7 – Electron- and hole-dominant devices

To further investigate the charge-injection and transport properties in PhOLEDs containing solution-processed ETL doped with alkali metal salts (M_2CO_3 , $\text{M} = \text{Cs, Li}$), two types of single-carrier dominant devices were fabricated, including electron-dominant devices, ITO/polymer host (70 nm)/solution-deposited BPhen: M_2CO_3 ETL (20nm)/Al, and hole-dominant devices, ITO/PEDOT:PSS (30 nm)/polymer host (70 nm)/solution-deposited BPhen: M_2CO_3 ETL (20 nm)/Au. The polymer host consisted of PVK and OXD-7 with the same ratio of 6:4 as in the PhOLEDs, except that the blue triplet emitter FIrpic was excluded. It is assumed that hole-injection from the ITO can be suppressed by the large energy barrier between the work function of ITO ($\Phi_f = \sim 4.5$ eV) and the ionization potential (IP) values of the polymer host (5.8 eV for PVK and 6.2 eV for OXD-7) in the electron-dominant devices. Similarly, electron-injection can be prevented by the energy barrier between the work function of Au ($\Phi_f = 5.0$ eV) and the electron affinity (EA) of BPhen (3.0 eV) in the hole-dominant devices.

Figure 9 shows the single charge carrier-dominant devices with solution-processed BPhen: M_2CO_3 ETL with varying concentration of the M_2CO_3 dopants ($\text{M} = \text{Cs, Li}$). The J - V characteristics of the electron-dominant devices with solution-processed BPhen ETL doped with Cs_2CO_3 and Li_2CO_3 are shown in **Figure 9a and 9b**, respectively. A significant increase of the current density was observed when the BPhen ETL was doped by the alkali metal salt

in electron-dominant devices. As shown by the highest current densities, the electron-injection and transport was the most efficient when the Cs_2CO_3 and Li_2CO_3 doping concentrations were 10.0 wt% and 5.0 wt%, respectively. This trend matches well with the observed highest performance of PhOLEDs with BPhen doped with alkali metal salt. These results imply that electron-injection and transport are enhanced by incorporating alkali metal salt into the ETL, achieving the maximum current density at optimum concentration of the alkali metal salt. However, further increase of the M_2CO_3 dopant concentration (12.5 and 15.0 wt% for Cs_2CO_3 , 7.5 and 10.0 wt% for Li_2CO_3) results in decrease of the current density. The trend also matches with the observed decrease PhOLED performance at the higher doping levels, presumably due to the phase separation in the solution-processed BPhen: M_2CO_3 blend ETLs which interrupts facile electron-injection and transport.

The J - V characteristics of the hole-dominant devices containing the solution-processed BPhen ETL doped with Cs_2CO_3 and Li_2CO_3 are shown in **Figure 9c and 9d**, respectively. The trends are similar to those for electron-dominant devices in that increased current density is seen with incorporation of alkali metal salt doped ETL. It has been reported that devices with BPhen ETL doped with Li_2CO_3 by vacuum co-deposition showed reduced hole-current as the dopant concentration increased. In contrast, the solution-processed BPhen ETL doped with alkali metal salt show enhanced hole-current and this can be understood to result from a good contact between the ETL and Au electrode enabled by solution-processing. This result implies that the strategy applied to improve charge-injection and transport by tuning the surface morphology of the ETMs to improve the interfacial contact between the ETL and metal cathode is not limited to Al, but can also be applied to other metal electrodes. On the other hand, the current density of the hole-dominant devices is reduced at higher concentrations of the dopant (Cs_2CO_3 = 12.5 - 15.0 wt%, Li_2CO_3 = 10.0 wt%), presumably due to the reduced charge-injection and transport when phase separation occurs in the BPhen: M_2CO_3 blend ETL. This means that for a given electron-transport material there might be an optimum alkali metal salt doping level for maximum PhOLED performance.

Example 8 – Space-charge-limited current (SCLC) measurement of solution-processed BPhen ETLs

Further investigated are the electron transport properties of the solution-processed alkali metal salt doped BPhen ETL films by space-charge-limited current (SCLC) measurement. The current-voltage (I - V) characteristics of the SCLC devices with the

structure of ITO/ETL(~ 200 nm)/Al, are shown in **Figure 10**. The BPhen:M₂CO₃ blend ETLs were spin coated from FA:H₂O (3:1) solutions with different concentrations of the alkali metal salts to form ~ 200 -nm thick layers, which were vacuum dried overnight at 50°C followed by Al deposition. The thickness of the BPhen ETLs was measured by a profilometer and also confirmed by AFM measurement. The electron mobility was extracted by fitting the J - V curves in the near quadratic region according to the modified Mott-Gurney equation,

$$J = \frac{9}{8} \epsilon \epsilon_0 \mu \frac{V^2}{L^2} \exp\left(0.899 \frac{\sqrt{V}}{\sqrt{L}}\right)$$

where J is the current density, ϵ_0 is the permittivity of free space, ϵ is the relative permittivity, μ is the zero-field mobility, V is the applied voltage, L is the thickness of active layer, and β is the field-activation factor (**Table 3**). The zero-field electron mobility of the solution-deposited BPhen:M₂CO₃ blend films varied from $4.2 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ without doping, which is consistent with the reported value by SCLC measurement, to $3.7 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ when the doping concentration is 10.0 wt% Cs₂CO₃ (**Figure 10a**, **Table 3**). The electron mobility of BPhen with 10.0 wt% Cs₂CO₃ was an order of magnitude higher than that with 5.0 wt% Cs₂CO₃ and two orders of magnitude higher than the non-doped BPhen. Similarly, BPhen doped with 2.5 – 5.0 wt% Li₂CO₃ had two orders of magnitude higher mobility ($1.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) than that of non-doped BPhen.

However, further increase of the doping concentration to 15.0 wt% for Cs₂CO₃ and 10.0 wt% for Li₂CO₃, resulted in the electron mobilities dropping to 1.8×10^{-5} and $7.5 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. Interestingly, I - V curves of the SCLC devices with the highest doping concentrations (15.0 wt% Cs₂CO₃, 7.5 - 10.0 wt% Li₂CO₃) showed steep slopes at high electric field, implying that the current increases faster than V^2 . These curvatures indicate the presence of charge trapping sites, which likely originate from the phase separated morphology of the solution-processed BPhen:M₂CO₃ blend ETLs.

Table 3. SCLC electron mobility of BPhen ETL at various doping levels.

Dopant	concentration [wt%]	L [nm]	β [cm ^{1/2} V ^{-1/2}]	E_{max} [V cm ⁻¹]	$\mu_e (E=0)$ [cm ² V ⁻¹ s ⁻¹]
None	0	200	8.7×10^{-6}	1.8×10^5	4.2×10^{-5}
Cs ₂ CO ₃	5.0	200	6.8×10^{-7}	1.8×10^5	5.6×10^{-4}
Cs ₂ CO ₃	10.0	200	8.3×10^{-6}	1.8×10^5	3.7×10^{-3}
Cs ₂ CO ₃	15.0	200	4.9×10^{-5}	1.8×10^5	1.8×10^{-5}
Li ₂ CO ₃	5.0	200	1.3×10^{-5}	1.5×10^5	1.3×10^{-3}
Li ₂ CO ₃	7.5	200	1.1×10^{-5}	1.5×10^5	1.0×10^{-3}
Li ₂ CO ₃	10.0	190	1.5×10^{-5}	1.6×10^5	7.4×10^{-5}

Example 9 – PhOLEDs with doped BPhen ETLs – Various Metals for the Dopant

To further test the approach of solution-processing of metal salt doped ETL, metal salt dopants with different metals were investigated, including Lithium carbonate (Li₂CO₃), sodium carbonate (Na₂CO₃), potassium carbonate (K₂CO₃), and cesium carbonate (Cs₂CO₃). The solution-processed ETL was doped with 10.0 mol% dopant and incorporated into multilayered blue PhOLEDs as described in Example 2.

As shown in **Figure 11**, various metal salts are suitable as n-type dopants in solution-deposited BPhen ETL. Li₂CO₃, Na₂CO₃, K₂CO₃, and Cs₂CO₃ work as good n-type dopants with BPhen electron-transport material to solution-deposit doped ETL in blue PhOLEDs. The dopant concentration was fixed at 10.0 mol%. The solution-processed PhOLEDs have the following structures:

Device I: ITO/PEDOT:PSS/Blue EML/solution-processed BPhen/Al;

Device II: ITO/PEDOT:PSS/Blue EML/solution-processed BPhen:Li₂CO₃/Al;

Device III: ITO/PEDOT:PSS/Blue EML/solution-processed BPhen:Na₂CO₃/Al;

Device IV: ITO/PEDOT:PSS/Blue EML/solution-processed BPhen:K₂CO₃/Al; and

Device V: ITO/PEDOT:PSS/Blue EML/solution-processed BPhen:Cs₂CO₃/Al.

The metal salt dopants with different metals all acted as efficient n-type dopants showing enhanced device performance compared to the device with BPhen without dopant (device I) as shown in **Figure 11**. The devices with solution-processed BPhen ETL doped with Na₂CO₃, K₂CO₃, and Cs₂CO₃ showed significantly enhanced device performance with

luminous efficiency (LE) values (30.0 - 33.7 cd/A, 9.6 – 12.7 lm/W) compared to the device without dopant (14.8 cd/A, 3.9 lm/W).

Example 10 – PhOLEDs with doped BPhen ETLs – Various Anions for the Dopant

To further test the approach of solution-processing of metal salt doped ETL, metal salt dopants with different anions were investigated, including cesium carbonate (Cs_2CO_3), cesium oxalate ($\text{Cs}_2(\text{COO})_2$) and cesium formate (CsHCO_2). The solution-processed ETL was doped with 7.5 mol% dopant and incorporated into multilayered blue PhOLEDs as described in Example 2.

For vacuum co-evaporated ETL, cesium oxalate ($\text{Cs}_2\text{C}_2\text{O}_4$) has not been considered as a suitable n-type dopant. See e.g., Wemken *et al.*, *J. Appl. Phys.* **2012**, *111*, 074502; Schmid *et al.*, “Structure Property Relationship of Salt-based n-Dopants in Organic Light Emitting Diodes”, The Fifth Organic Electronics Conference and Exhibition (OEC 07), September 24-26, 2007, Frankfurt, Germany.

However, as shown in **Figure 12**, cesium oxalate ($\text{Cs}_2(\text{COO})_2$) and cesium formate (CsHCO_2) work as good n-type dopants with BPhen electron-transport material to solution-deposit doped ETL in blue PhOLEDs. The dopant concentration was fixed at 7.5 mol%. The solution-processed PhOLEDs have the following structures:

Device I: ITO/PEDOT:PSS/Blue EML/solution-processed BPhen/Al;

Device II: ITO/PEDOT:PSS/Blue EML/solution-processed BPhen: Cs_2CO_3 /Al;

Device III: ITO/PEDOT:PSS/Blue EML/solution-processed BPhen: $\text{Cs}_2(\text{COO})_2$ /Al; and

Device IV: ITO/PEDOT:PSS/Blue EML/solution-processed BPhen: CsHCO_2 /Al.

As shown in **Figure 12**, the metal salts with different anions all acted as efficient n-type dopants showing enhanced device performance compared to the device with BPhen without dopant. The devices comprising solution-processed BPhen ETL doped with cesium oxalate showed the highest performance (27.0 cd/A, 9.9 lm/W) compared to the BPhen ETL without dopant (13.3 cd/A, 3.3 lm/W). Blue PhOLEDs with cesium carbonate or cesium formate dopant also showed enhanced device performance. These results demonstrated that cesium oxalate works even better than cesium carbonate as n-type dopant of a solution-deposited ETL, in sharp contrast to the conclusion of the prior art ETL obtained by vacuum co-evaporation. These results also proved that the solution-processing of metal salt doped ETL can be achieved by metal salt dopants with various anions, including those that do not perform well in vacuum co-evaporated ETL.

WHAT IS CLAIMED IS:

1. A composition suitable for being deposited by solution processing to form an electron transporting layer of an electronic device, said composition comprising: (i) at least one electron transporting material having a molecular weight of 5,000 g/mol or less; (ii) at least one metal ion compound dopant of the electron transporting material; and (iii) one or more solvents capable of dissolving the electron transporting material and the dopant.
2. The composition of claim 1, wherein the electron transporting material has a molecular weight of 2,000 g/mol or less.
3. The composition of claim 1 or 2, wherein the electron transporting material comprises at least one 5-membered or 6-membered conjugated ring comprising at least one nitrogen heteroatom.
4. The composition of claim 3, wherein the nitrogen heteroatom is present in protonated form.
5. The composition of claim 1 or 2, wherein the electron transporting material comprises at least one conjugated ring selected from pyrrole, pyrazole, imidazole, oxazole, oxadiazole, triazole, indole, iso-indole, pyridine, pyrimidine, pyrazine, triazine, tetrazine, quinoline, iso-quinoline, and phenanthroline.
6. The composition of claim 1 or 2, wherein the electron transporting material is 1,3,5-tris(*m*-pyrid-3-yl-phenyl)benzene (TmPyPB), 1,3-bis(3,5-di(pyridine-3-yl)phenyl)benzene (BmPyPB), 1,3,5-(tris(4-pyridinquinolin-2-yl)benzene (TPyQB), 1,3,5-tris(4-phenylquinolin-2-yl)benzene (TQB), 1,3,5-tris(4-methylquinolin-2-yl)benzene (TMQB), 1,3,5-tris(4-(4-fluorophenyl)quinolin-2-yl)benzene (TFQB), 4,7-diphenyl-1,10-phenanthroline (BPhen), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), tris(2,4,6-trimethyl-3-(pyridine-3-yl)phenyl)borane (3TPyMB), 2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole (TPBI), 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD), 1,3-bis(2-(4-*tert*-butylphenyl)-1,3,4-oxadiazole-5-yl)benzene (OXD-7), 2,4,6-tris(diphenylamino)-1,3,5-triazine (TRZ), or a combination thereof.
7. The composition of any of claims 1-6, wherein the dopant is an alkali or alkaline earth metal ion compound represented by MX, M₂X, M₃X or MX₂, wherein M is Li, Na, K, Cs, Rb, Ca, Mg, Ba or Sr, and wherein X is OH, F, Cl, Br, CO₃, HCO₃, C₂O₄, SO₄, PO₄, BH₄, CN or RCOO, R is hydrogen or a C₁-C₃ optionally substituted alkyl or aryl.

8. The composition of claim 7, wherein the dopant is Li_2CO_3 , Cs_2CO_3 , Na_2CO_3 , K_2CO_3 , $\text{Cs}_2\text{C}_2\text{O}_4$, or CsHCO_2 .
9. The composition of any of claims 1-8, wherein the composition comprises a first polar solvent and a second polar solvent different from the first polar solvent.
10. The composition of claim 9, wherein the first polar solvent is water or a C_1 - C_3 alcohol, and wherein the second polar solvent is C_1 - C_4 carboxylic acid optionally substituted with one or more fluorine.
11. The composition of claim 10, wherein the first polar solvent is water, wherein the second polar solvent is formic acid, and wherein the molar ratio of water to formic acid is between 1:1 and 1:9.
12. The composition of any one of the preceding claims, wherein the weight of the dopant, based on the total weight of the electron transporting material and of the dopant, is between 0.1% and 20%.
13. A method, comprising:
 - providing the composition according to any one of the preceding claims; and
 - depositing said composition by solution processing and drying to form an electron transporting layer of an electronic device.
14. The method of claim 13, wherein the electron transporting layer is formed under air and at a temperature lower than 100°C .
15. The method of claim 13 or 14, wherein the composition is deposited over an active layer of an electronic device, and wherein the active layer is not solvated during the solution processing of the electron transporting layer.
16. A method for manufacturing an electronic device, comprising
 - depositing an active layer of the electronic device by solution processing, then
 - applying the method of claim 15 to form the electron transporting layer of the electronic device.
17. An electronic device, comprising:
 - (i) an active layer, optionally susceptible of being formed by solution processing; and
 - (ii) an electron transporting layer obtained by the method of any of claims 13-16.
18. The electronic device according to claim 17, wherein the electronic device is an electroluminescence device, a photovoltaic device, or a field-effect transistor.

19. The electronic device of claim 17 or 18, wherein the electronic device is an OLED device comprising at least one phosphorescent emitter dispersed in a host material having a molecular weight of 5,000 g/mol or less as the active layer, and wherein the OLED device has an external quantum efficiency of at least 10% at 1,000 cd/m².
20. A composition suitable for being deposited by solution processing to form an electron transporting layer of an electronic device, said composition being preparable by combination of: (i) at least one electron transporting material having a molecular weight of 5,000 g/mol or less; (ii) at least one metal ion compound dopant of the electron transporting material; and (iii) one or more solvents capable of dissolving the electron transporting material and the dopant.
21. A composition preparable by:
- (A) combining: (i) at least one electron transporting material having a molecular weight of 5,000 g/mol or less; (ii) at least one metal ion compound dopant of the electron transporting material; and (iii) one or more solvents capable of dissolving the electron transporting material and the dopant; to form a first composition, and
 - (B) forming a film from the first composition by removing solvent.
22. A method for preparing a composition suitable for being deposited by solution processing to form an electron transporting layer of an electronic device, which comprises combining: (i) at least one electron transporting material having a molecular weight of 5,000 g/mol or less; (ii) at least one metal ion compound dopant of the electron transporting material; and (iii) one or more solvents capable of dissolving the electron transporting material and the dopant.
23. A method for obtaining a second composition, comprising forming a film from a first composition by removing solvent, wherein the first composition which is the composition prepared by the method according to claim 22.
24. A method for preparing a second composition, comprising:
- combining: (i) at least one electron transporting material having a molecular weight of 5,000 g/mol or less; (ii) at least one metal ion compound dopant of the electron transporting material; and (iii) one or more solvents capable of dissolving the electron transporting material and the dopant, so as to obtain a first composition; and
 - forming a film from the first composition by removing solvent, so as to obtain the second composition.

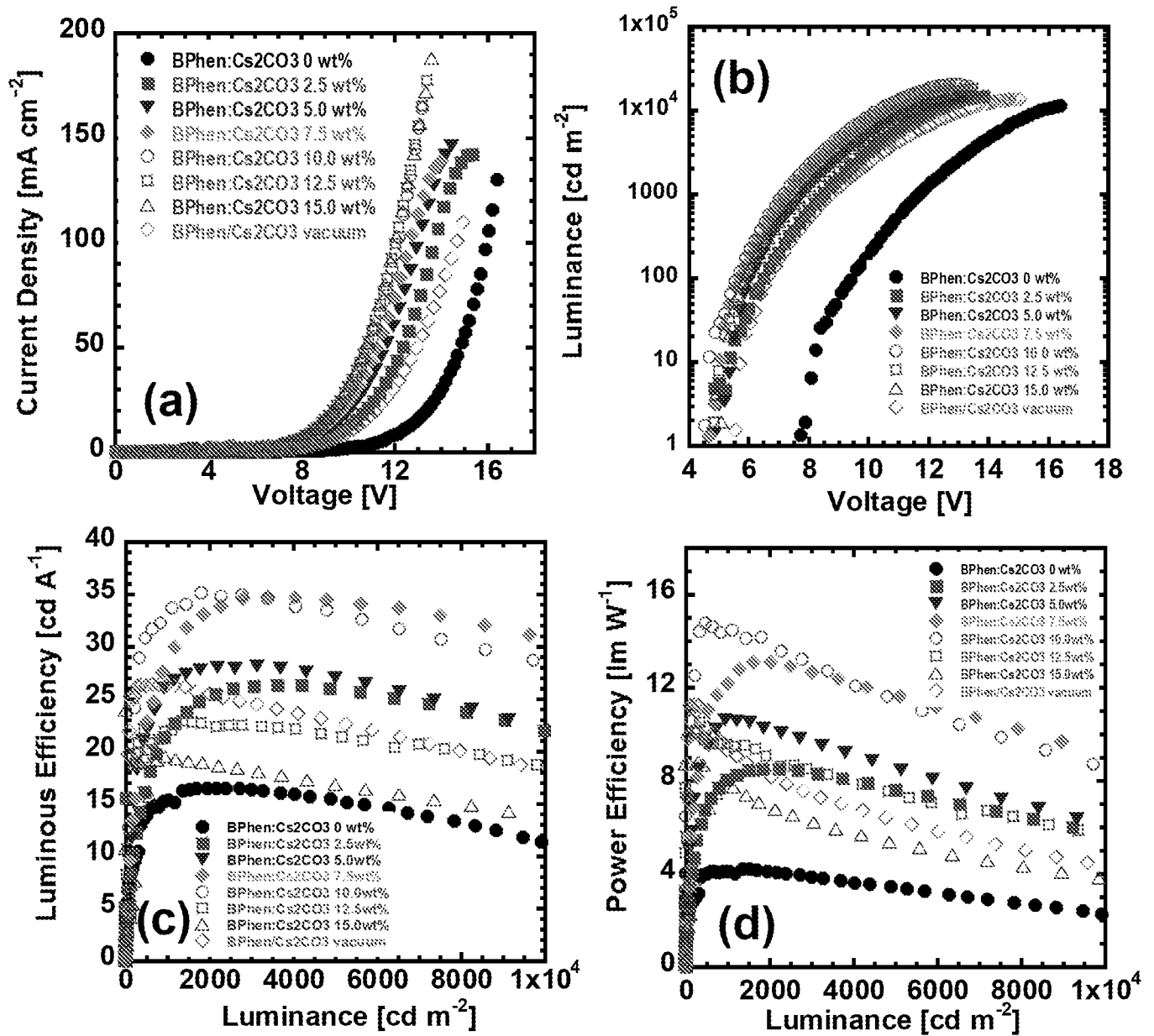


FIGURE 1

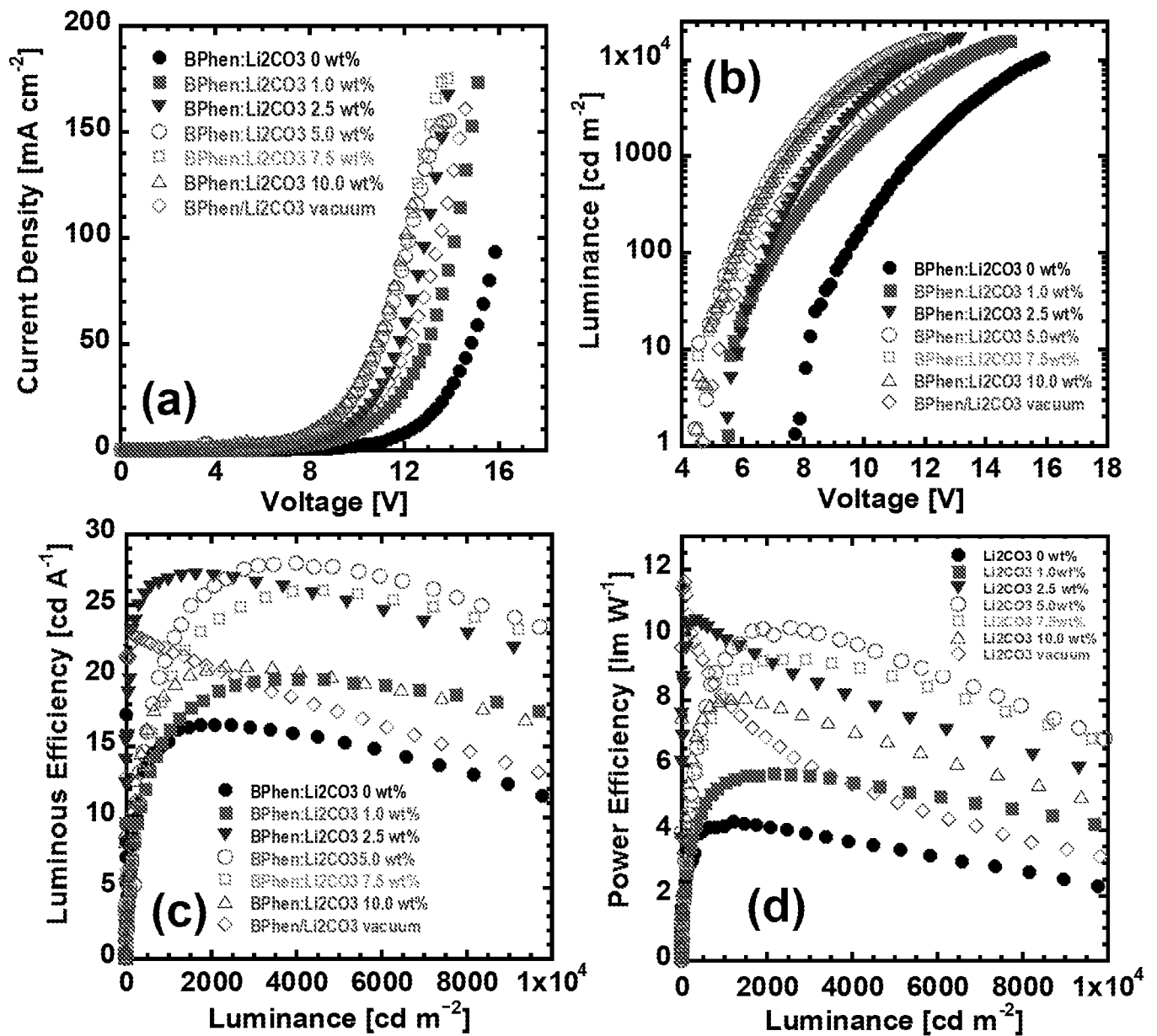


FIGURE 2

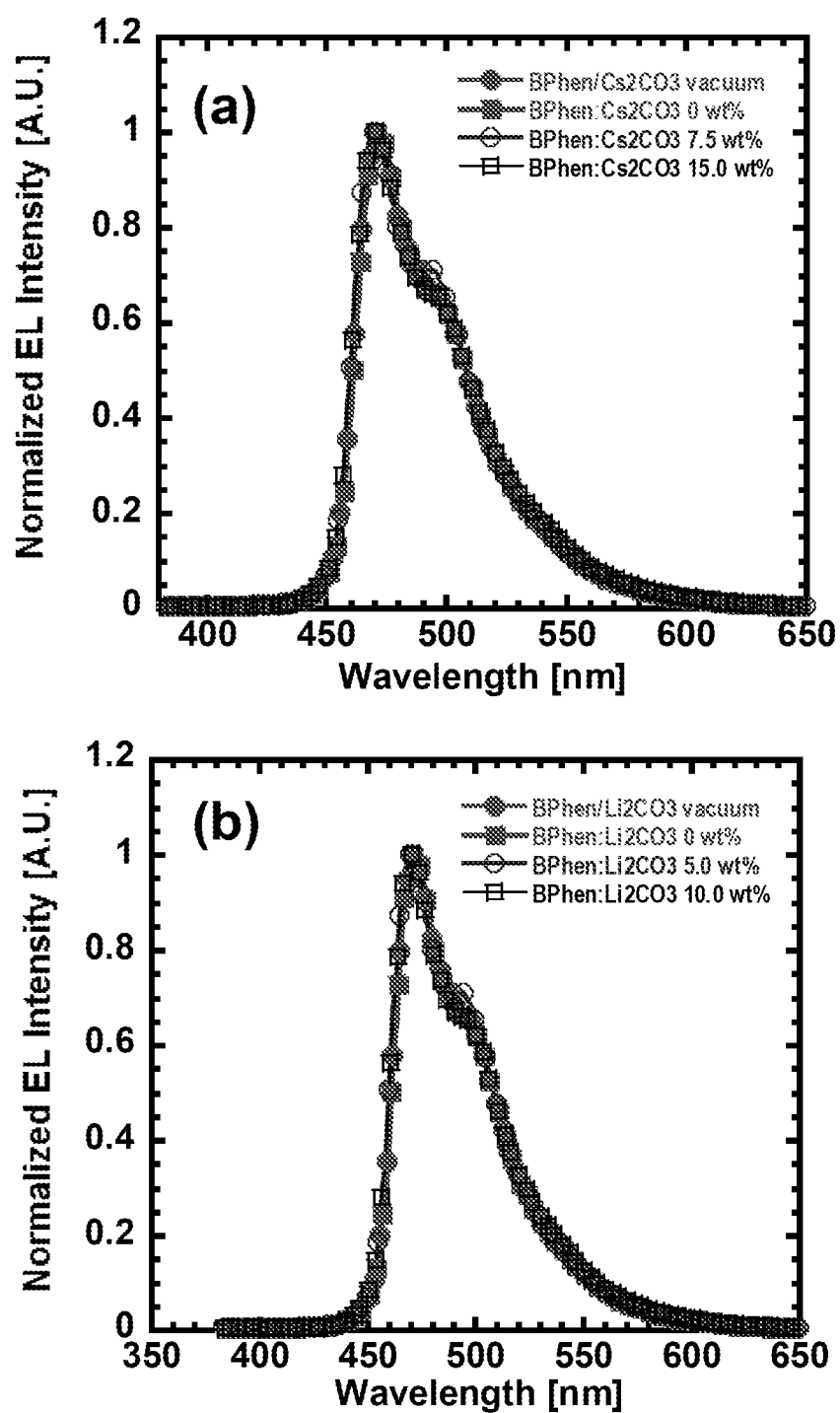


FIGURE 3

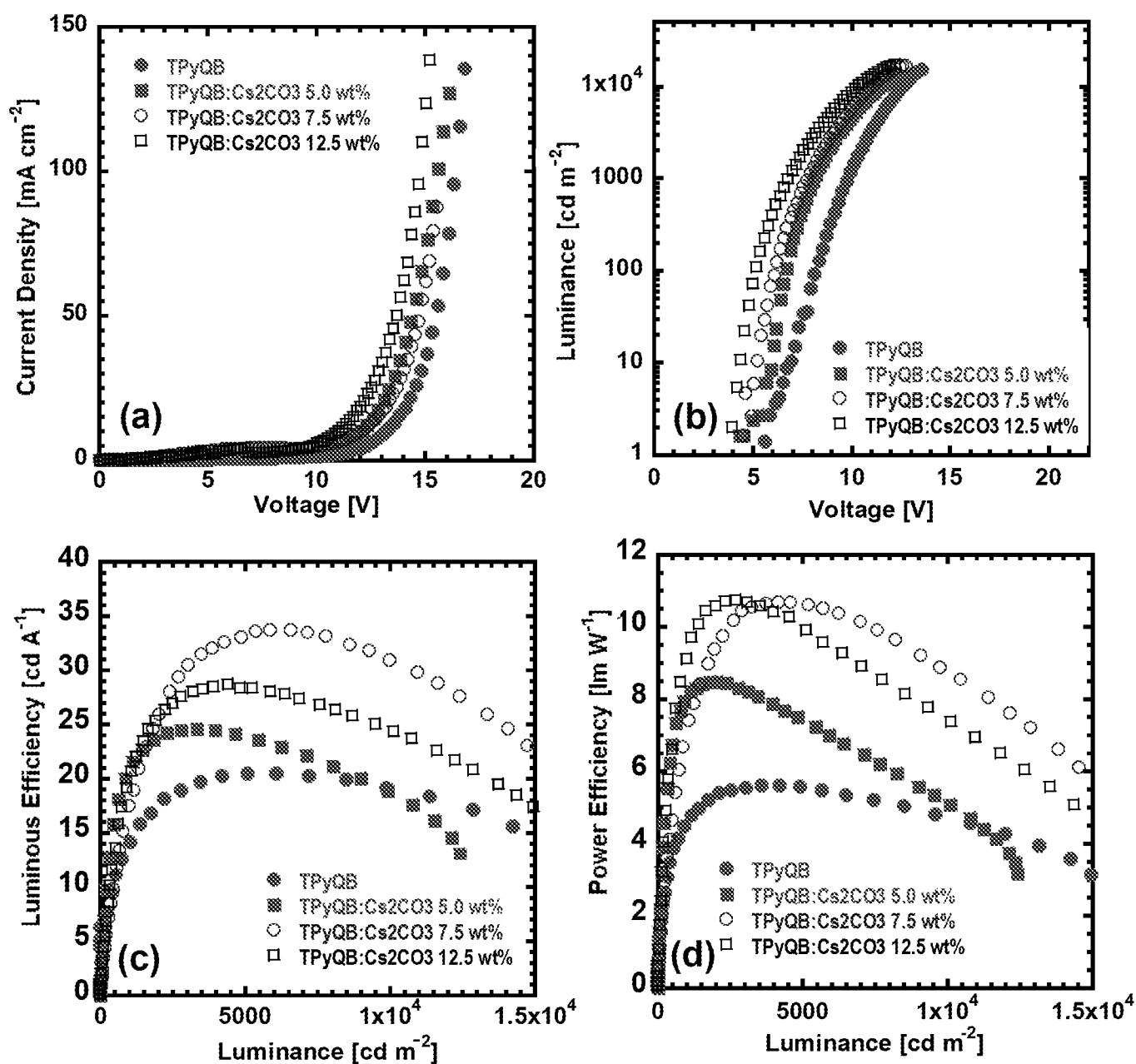


FIGURE 4

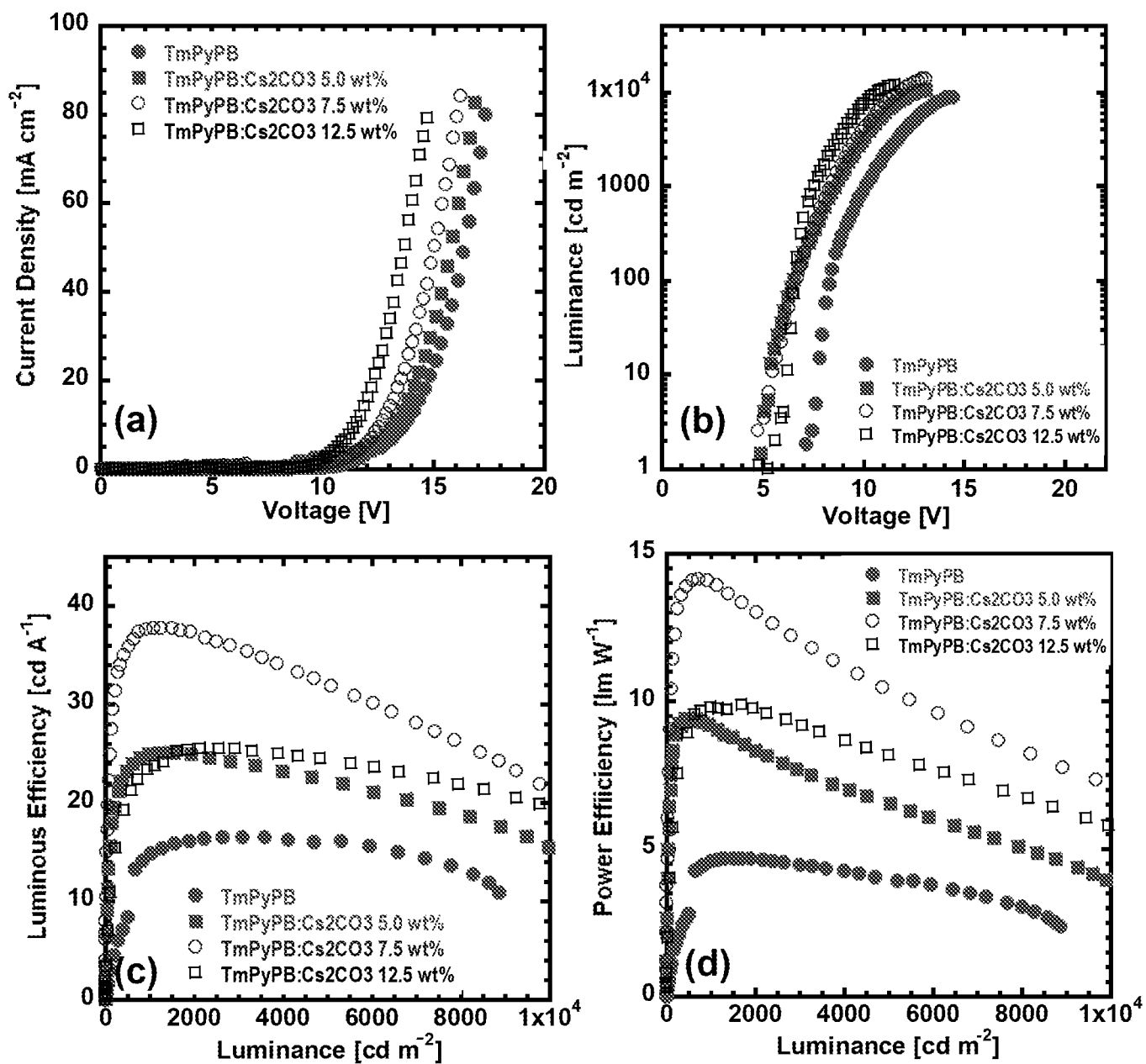


FIGURE 5

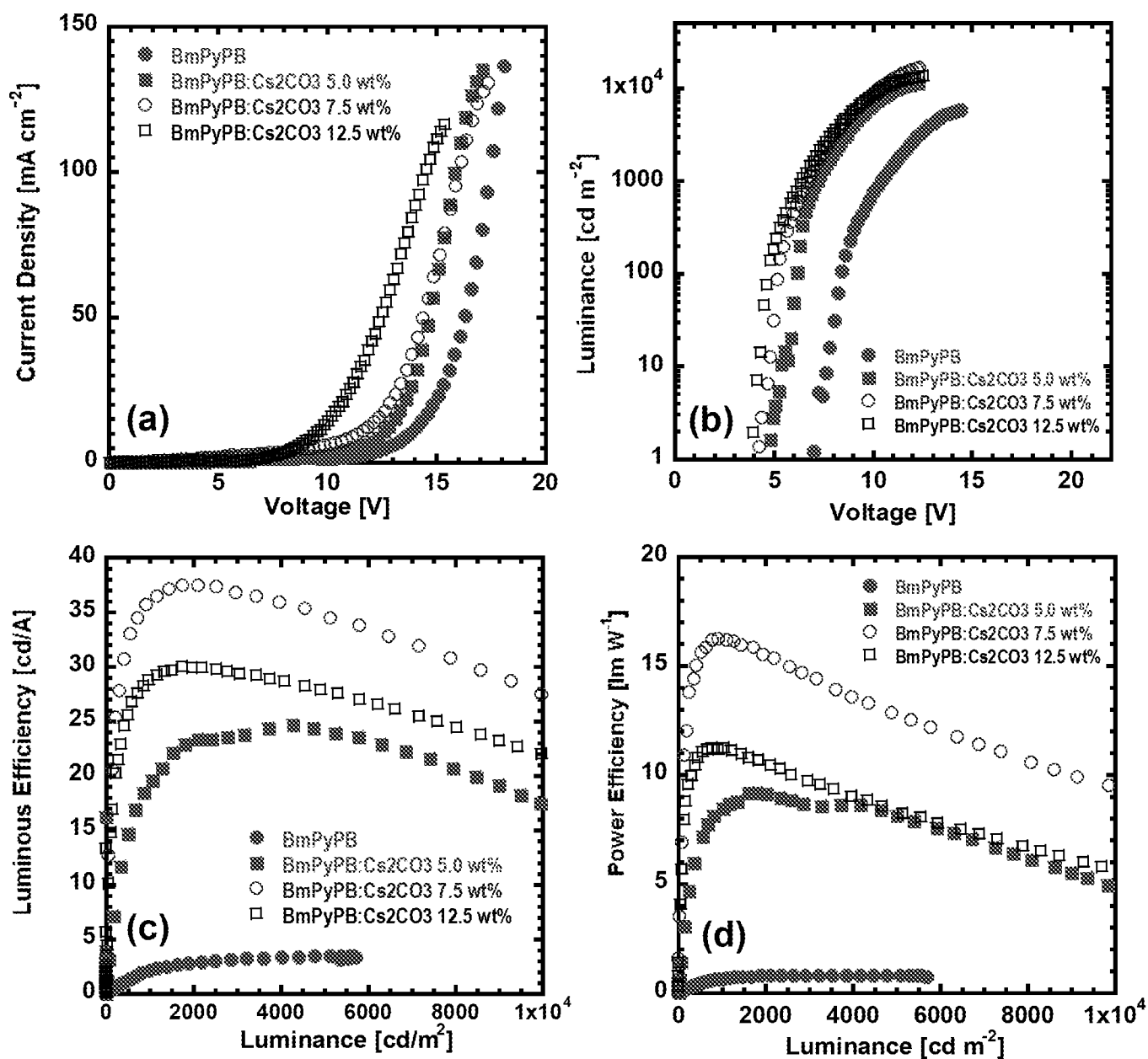


FIGURE 6

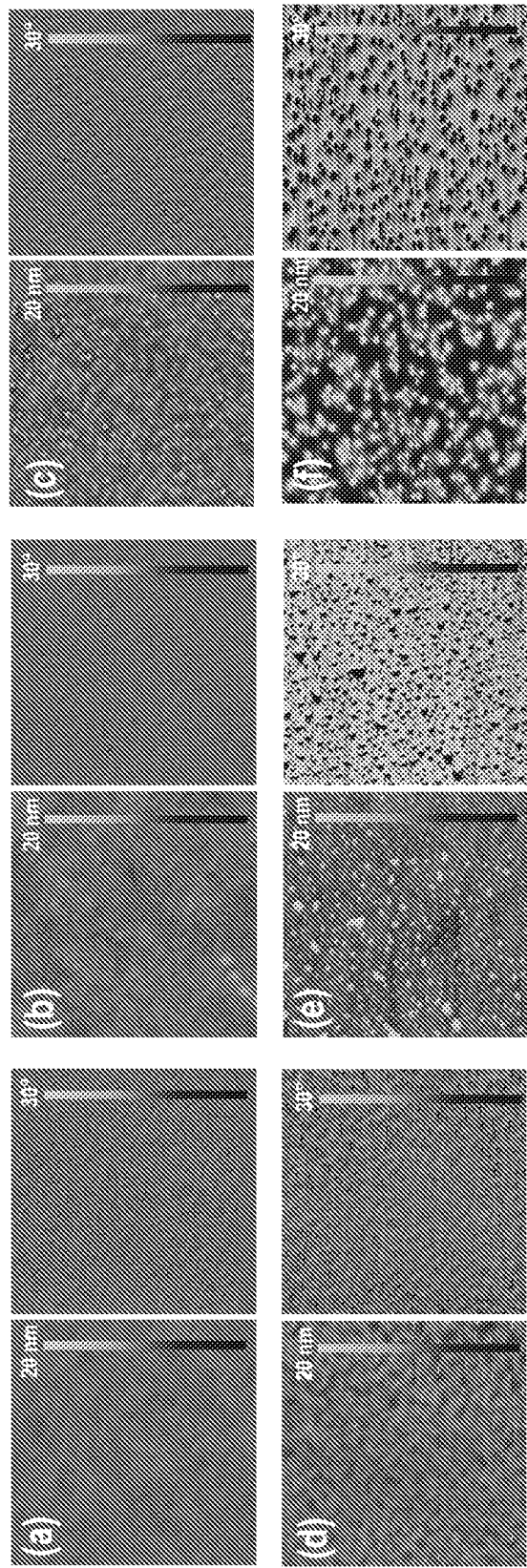


FIGURE 7

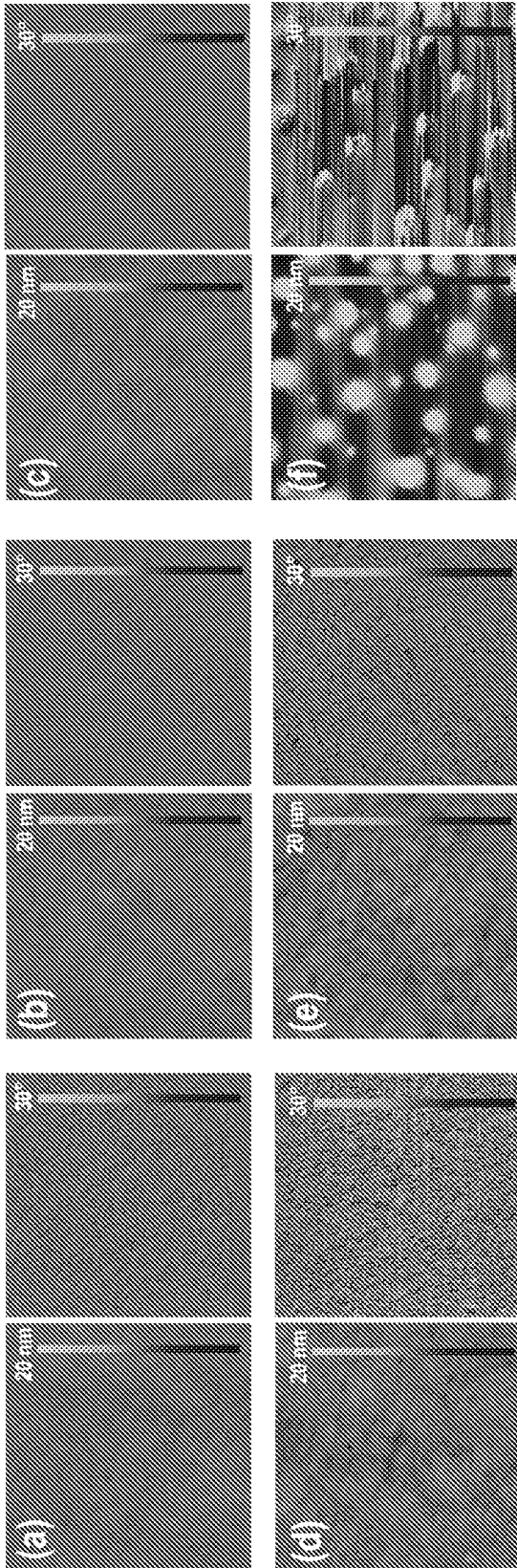


FIGURE 8

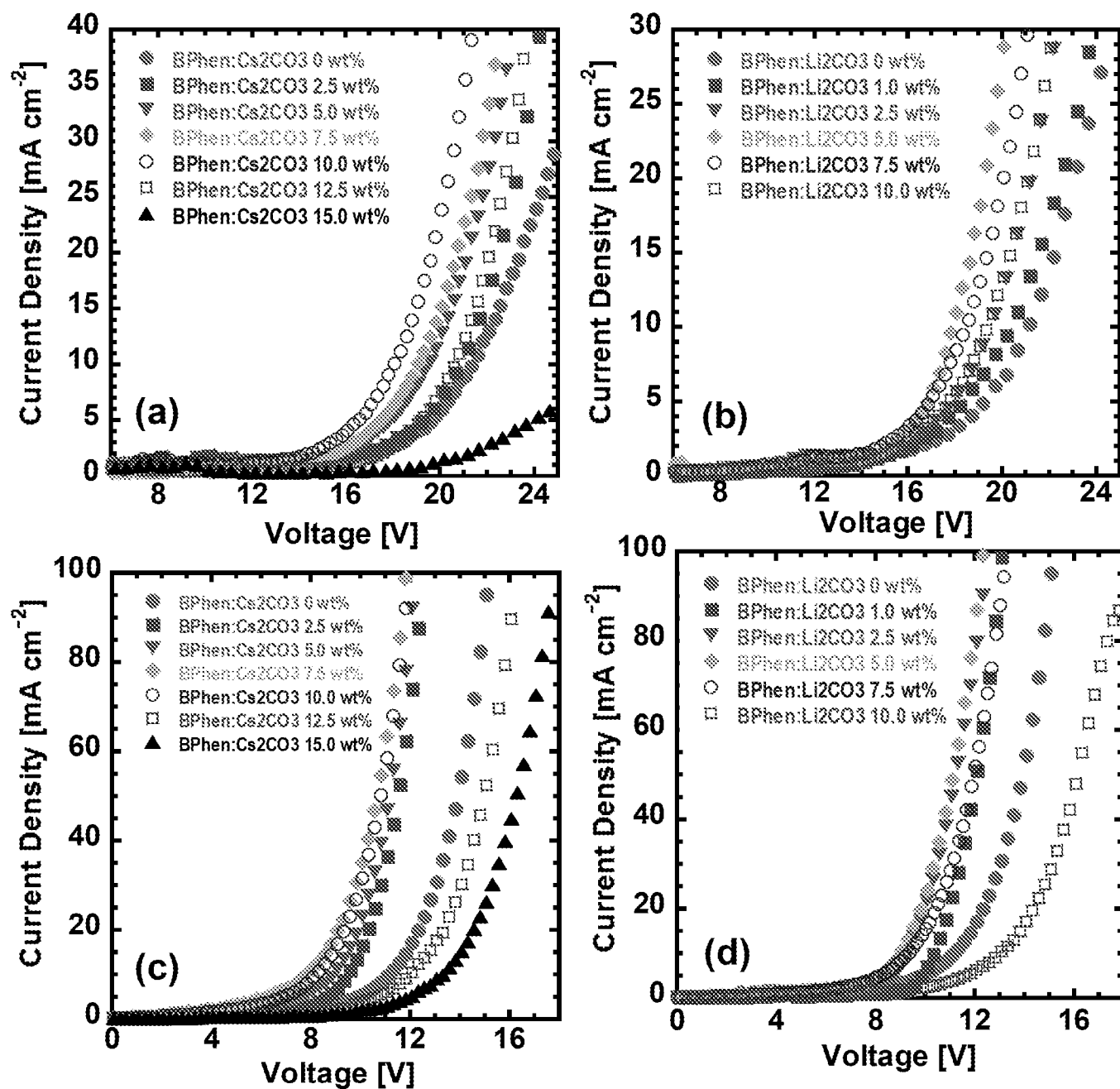


FIGURE 9

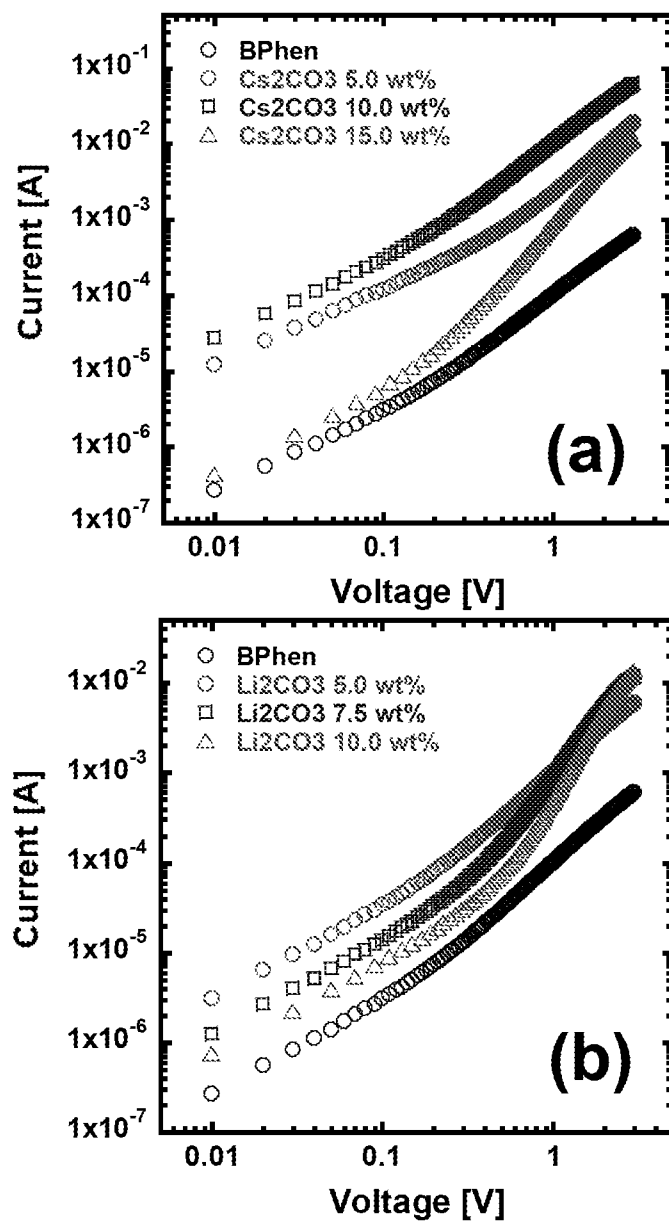


FIGURE 10

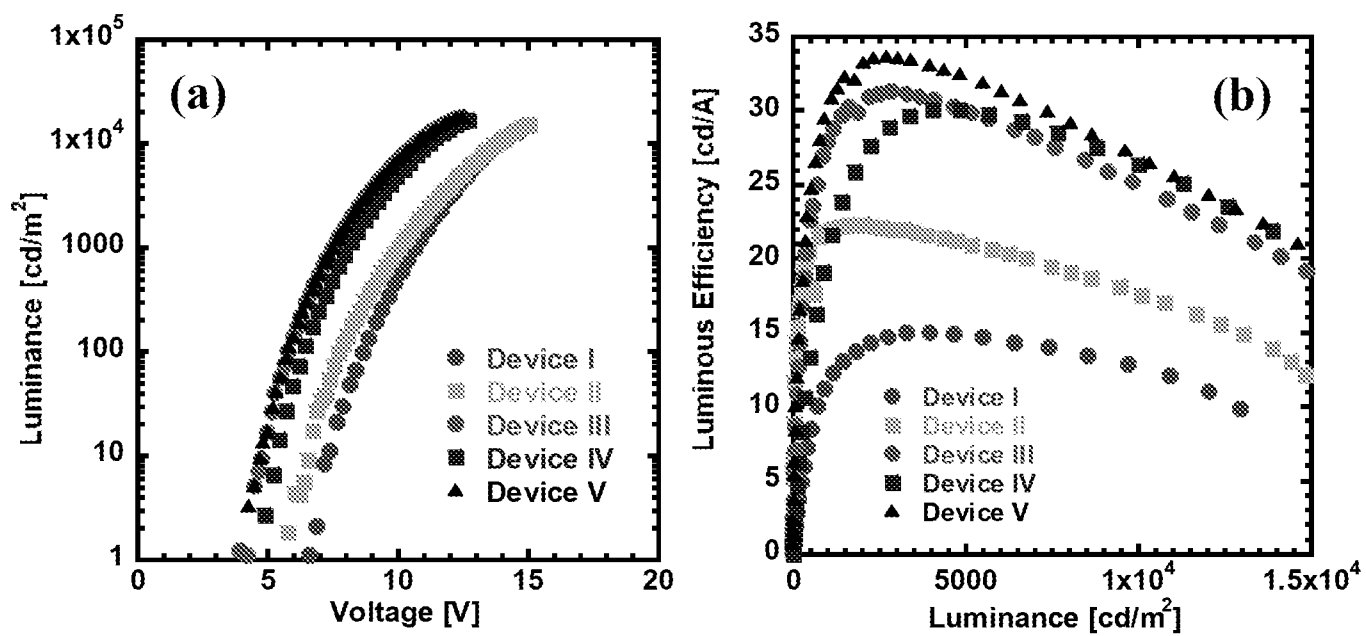


FIGURE 11

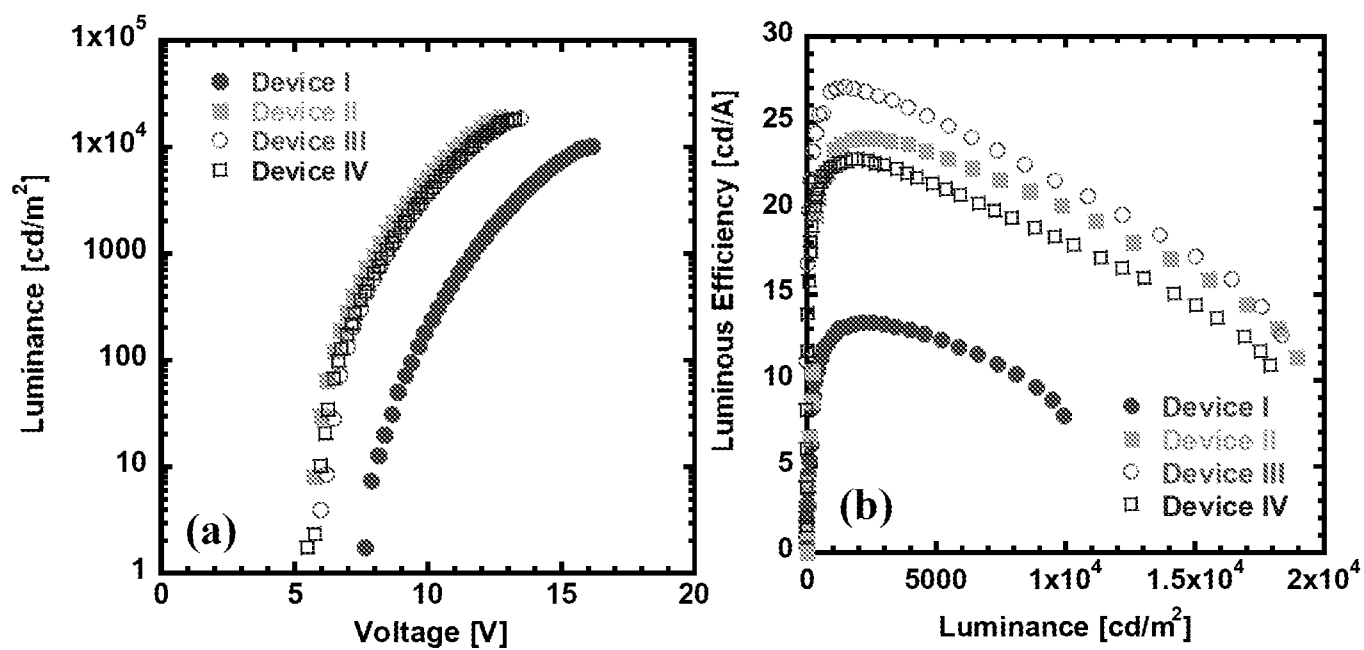


FIGURE 12

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/044591

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01L51/50
ADD. H01L51/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EP0-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LEE D H ET AL: "Effect of hole transporting materials in phosphorescent white polymer light-emitting diodes", ORGANIC ELECTRONICS, ELSEVIER, AMSTERDAM, NL, vol. 11, no. 3, 1 March 2010 (2010-03-01), - 29 November 2009 (2009-11-29), pages 427-433, XP026888753, ISSN: 1566-1199, DOI: 10.1016/J.ORGEL.2009.11.022 [retrieved on 2009-11-26] page 428 abstract	1-24
X	WO 2011/158592 A1 (KONICA MINOLTA HOLDINGS INC [JP]; KONUMA TARO [JP]; MUROTA KAZUTOSHI []) 22 December 2011 (2011-12-22) paragraphs [0089] - [0097] paragraphs [0168] - [0186]; tables 1,2 -/--	1-24



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

22 August 2013

Date of mailing of the international search report

29/08/2013

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INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P	& US 2013/087778 A1 (KONUMA TARO [JP] ET AL) 11 April 2013 (2013-04-11) paragraphs [0089] - [0097] paragraphs [0168] - [0186]; tables 1,2 -----	1-24
X	US 2011/284825 A1 (YANG MINYANG [KR] ET AL) 24 November 2011 (2011-11-24)	1,2,7-24
A	paragraphs [68+96] - [0117]; figure 4 -----	3-6

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2013/044591

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2011158592 A1	22-12-2011	US 2013087778 A1 WO 2011158592 A1	11-04-2013 22-12-2011
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