Front. Optoelectron. China 2009, 2(4): 435–441
DOI 10.1007/s12200-009-0064-2

RESEARCH ARTICLE

Charge balance materials for homojunction and heterojunction OLED applications

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Abstract In a homojunction device, a single organic layer assumes the multiple roles of hole, electron transportation, and emitter. Its ease in processing is highly desirable from the manufacturing point of view. In this paper, we shall describe the synthesis of a range of bipolar small molecules and conductive vinyl polymers for application in homojunction and heterojunction organic light emitting diodes (OLEDs). The bipolar materials, in general, consist of three basic building blocks: an arylamine, a 1,3,4-oxadiazole, and a polycyclic aromatic moiety. The achievement of charge balance can be validated either by direct measurement of electron/hole mobility or indirectly via optimization of device properties. A series of conductive vinyl copolymers containing hole transporting *N*-(4-methoxyphenyl)-*N*-(4-vinylphenyl) naphthalen-1-amine (4MeONPA) and electron transporting 2-phenyl-5-(4-vinylphenyl)-1,3,4-oxadiazole (OXA) at different compositions was applied for heterojunction and homojunction OLEDs. For heterojunction devices employed the copolymers as the hole transporting layer and Alq_3 as the electron transporting and emitting layer, a maximum luminance and current efficiency of over 23000 cd/m^2 and 4.2 cd/A (PL of Alq_3), respectively, were achieved at the charge balance composition. Homojunction devices for the copolymers were demonstrated by the addition of rubrene as a dopant. The single layer devices at the optimal copolymer composition has ca 1500 cd/m^2 and 0.74 cd/A.

Keywords homojunction devices, charge balance, bipolar small molecules, conductive vinyl copolymers

1 Introduction

The first commercially viable organic light emitting diodes (OLEDs) based on a multilayer design was reported by Tang et al. in 1987 [1]. Since then there have been tremendous advances both in design of novel materials and device configurations. The multilayer devices were known as heterojunction OLEDs, as the recombination of electron/hole pairs and formation of excitons occurred at the interface of the hole and electron transporting layers. In the design of high performance materials for electroluminescent applications, critical parameters such as emission efficiency, charge mobility and achievement of charge balance for the different layers must be considered [2,3]. The power efficiency of OLED based on fluorescent dyes is limited to the 25% singlet quantum states available. The application of phosphorescent dyes such as Ir complexes improved the efficiency drastically with the provision of additional available 75% triplet quantum states [4]. It is known that hole mobility of most arylamine compounds (e.g., TPD, NPB) are 1–2 orders higher than most electron transporting materials including the commonly used aluminum (III) quinolinate complex (Alq_3). Migration of excess holes into the Alq_3 layer can lead to the formation of unstable cationic species and was suggested as the cause for dark spot formation in Alq_3-based devices [5]. The build up of residual charge at the interface has also been suggested for mechanical failure in heterojunction OLEDs [6]. The attainment of charge balance not only improves stability for heterojunction OLEDs, it is also essential for the design of homojunction OLEDs.

Unlike heterojunction devices, homojunction OLEDs only employ a single layer for both hole and electron charge transportation. Its ease of processing is highly desirable from the manufacturing point of view. Imbalance in charge transport properties for homojunction devices would result in quenching of the excitons near surfaces of the metallic electrodes. We have previously reported the synthesis of several series of bipolar small molecules for homojunction OLED applications [7–9]. Effects on the variation of the arylamine chemistry and number of 1,3,4-oxadiazole electron transporting moiety have been investigated [7,8]. Subsequently, by increasing the size of the polycyclic aromatic moiety was found not only to have the

Received July 30, 2009; accepted September 17, 2009

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emission spectrum red-shifted, it also improved the device efficiency as a whole [9]. The achievement of charge balance can be verified by the overlapping of the hole and electron mobility data determined using a time-of-flight (TOF) mobility measurement method as well as from observed enhanced performance of the single layer homojunction devices [9].

Long term stability and ease in the manufacturing process are two of the critical requirements for commercialization of OLEDs. Polymer OLED (PLED) can best meet these challenges by adopting low production cost solution processing and thus the ability for making large area flexible panel. High molecular weight (MW) polymers with high glass transition temperature (Tg) can be used to produce thin films with excellent physical properties. Traditional main-chain conductive polymers have poor solubility at high MW, are absorptive in the visible range and are sensitive to degradation by oxygen and moisture. Side-chain conductive vinyl polymers, however, are highly soluble even at very high MW. Without long range pi electron delocalization, conductive vinyl polymers are optically clear and also less prone to environmental degradation. We have previously reported on the synthesis of a hole transporting conductive vinyl polymer, poly(*N*-phenyl-*N*-styryl-1-naphthylamine) (poly(NPA)) and its derivatives [10]. The vinyl conductive polymers have high MW (over 200000) yet are soluble in most common organic solvents (e.g., THF, chloroform, etc.). The polymers have high thermal stability (Tg above 160°C) and hole mobility approaching 10^{-3} cm^2/(V·s) using TOF measurement. The HOMO of the polymer has been found to be between 5.10 to 5.30 eV depending on the types of electron withdrawing or electron donating phenyl ring substitute group. Emission of the NPA-based PLEDs was blue and had EL maximum ranging from 424 to 450 nm. The vinyl monomer for this hole transporting NPA polymer can be used in combination with other electron transporting vinyl monomers to produce a range of bipolar conductive vinyl copolymers.

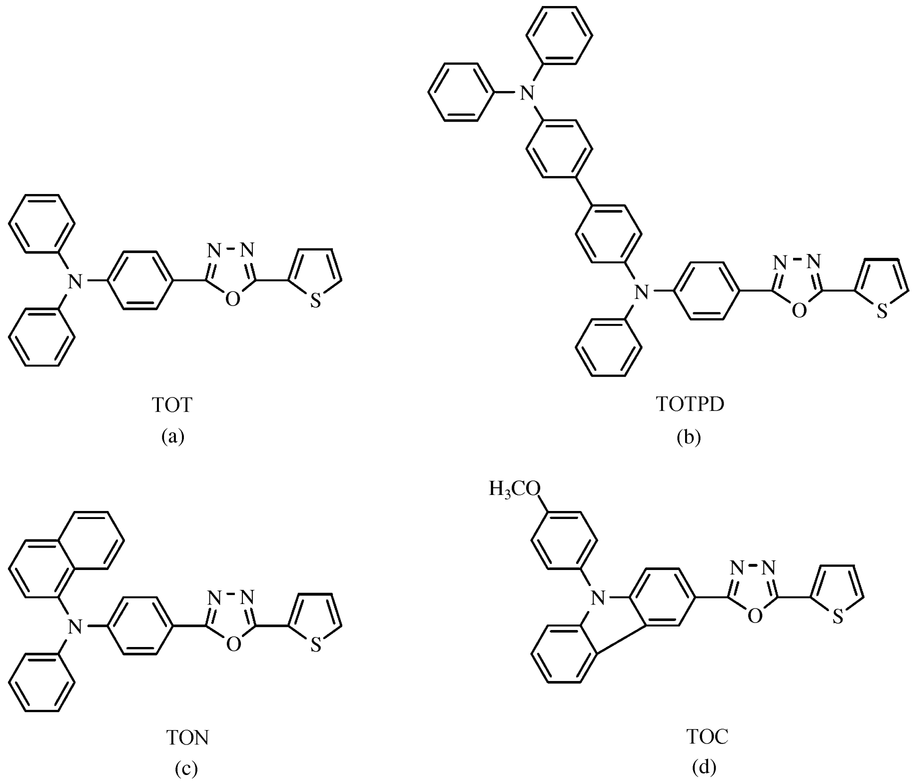
In this paper, we shall report the synthesis of several bipolar materials and its physical properties in correlation with their chemistry and compositions. Their applications in charge balance heterojunction and homojunction OLEDs will be demonstrated using a series of conductive vinyl copolymers. The correlation of their properties (physical/optical/electrical) relating to their chemistry and composition will be reported.

2 Experiment

The synthesis of a charge balance bipolar small molecule can be achieved by combining chemical moieties with different charge transport properties. Typically, arylamine is used for hole transporting and 1,3,4-oxadiazole for electron transporting. In the synthesis of thiophene-based bipolar small molecules with different arylamine moieties, an aldehyde was introduced to four different arylamines including triphenylamine (TPA), *N*,*N*′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (TPD), diphenyl(1-naphthyl)amine (NPA) and 9-phenylcarbazole (KPA) via a Vilsmeier-Haack formylation reaction [7]. The aldehyde was then converted to a cyanide group using hydroxylammonium chloride followed by sodium azide to produce the tetrazole intermediate. Thiophene-2-carbonyl chloride was then refluxed with the tetrazole to complete the 1,3,4-oxadiazole (OXD) ring formation [11]. The first series was to study the effects of the arylamine structure. Similarly, another bipolar small molecule series containing 2-phenylquinoline (PQ), a different number (n) of OXD and a diphenylamine (T) terminal group was prepared [8]. The small molecules, having the general structure PQ(OXD)$_n$T, $n=1,2,3$, were prepared by repeating the tetrazole intermediate formation step and termination with 2-phenylquinoline-4-carbonyl chloride. Finally, a series of donor-acceptor type compounds with the structure Ar-A-D was prepared in which A represented the electron deficient 1,3,4-oxadiazole (OXD) and D represented the electron rich triphenylamine (TPA) moiety. The effect on the size of the aromatic Ar moiety was studied by termination of the tetrazole intermediate with appropriate acid chloride based on the following aromatic structures containing the aromatic moiety phenyl, biphenyl, naphthyl, anthracenyl, pyrenyl, and acenaphtho[1,2-b]quinoxalinyl [9].

For the preparation of the conductive vinyl copolymers poly(NPA/OXD), the hole transporting MeONPA was prepared from *N*-phenylnaphthalen-1-amine using a modified Ullmann condensation reaction [12]. The aldehyde of MeONPA, 4-((4-methoxyphenyl naphthalen-1-yl)amino) benzaldehyde, was prepared using a Vilsmeier formylation reaction [13]. The resulting vinyl monomer was then produced with high yield via a Witting coupling reaction between the aldehyde and an ylide. The electron transporting 2-phenyl-5-(4-vinylphenyl)-1,3,4-oxadiazole monomer (OXD) was also obtained from a Wittig coupling reaction between the aldehyde, 4-(5-phenyl-1,3,4-oxadiazol-2-yl) benzaldehyde, and an ylide. The aldehyde was prepared from a ring closure reaction between 4-formylbenzoyl chloride and 5-phenyl-2H-tetrazole in pyridine also with good yield [13]. The copolymers were prepared through a solution free radical copolymerization using AIBN as the initiator and degassed toluene as the solvent at 80°C for hours using different monomer feed ratios.

The small molecules, monomers and their intermediates were purified by re-crystallization and analyzed using ^{1}H-NMR, FT-IR, GC-MS and elemental analysis. The polymers were purified by repeated re-precipitation and characterized by GPC, ^{1}H-NMR, FT-IR, DSC, TGA, UV-vis absorption, PL and cyclic voltammetry, etc. Preparation and measurement of the heterojunction and homojunction OLEDs have been reported in the past [14].



TOT
(a)

TOTPD
(b)

TON
(c)

TOC
(d)

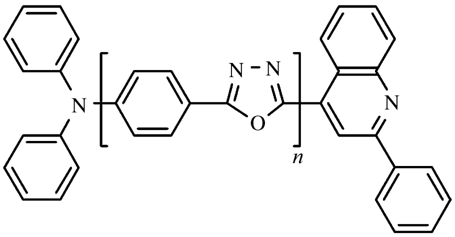
Fig. 1 Chemical structures of bipolar small molecules with different arylamine chemistry. (a) TOT; (b) TOTPD; (c) TON; (d) TOC

3 Results and discussion

3.1 Bipolar small molecules for homojunction devices

As we have suggested earlier, a bipolar and charge balance small molecules can be prepared by a combination of the three basic building blocks: an arylamine, a 1,3,4-oxadiazole and a polycyclic aromatic moiety. The contribution and performance of each of the basic component were studied in three bipolar small molecules series. In each of the series, the chemistry for one the basic building block was varied and its effect investigated. The first bipolar small molecules series (T-OXD-AA) consisted of a thiophene unit (T), a 1,3,4-oxadiazole unit (OXD) and four different arylamine (AA) moieties, as shown in Fig. 1. The arylamines studied included triphenylamine (TOT), *N*,*N*′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (TOTPD), diphenyl(1-naphthyl)amine (TON) and 9-phenylcarbazole (TOC). It was found that their HOMO ranged from 5.21 to 5.73 eV depending on the arylamine chemistry while their LUMO remained unchanged. Their corresponding emitting color varied from UV (393 nm) for TOC to bluish green (483 nm) for TOTPD. According to a cyclic voltammetry (CV), the compounds were mostly hole transporting while the one with TPD was bipolar with reversible anodic oxidation. The homojunction device prepared from TOTPD has over 2000 cd/m^2 in luminous intensity and a 1.10 cd/A maximum current efficiency [7].

The second bipolar small molecule series studied the effects of the number of OXD spacer units. The compounds (PQ(OXD)$_n$T, $n = 1,2,3$) contained 2-phenylquinoline (PQ), a different number (n) of OXD and a diphenylamine (T) terminal group, as shown in Fig. 2. It was found that although the Tg increased with n, the quantum efficiency decreased rapidly with n as well. The HOMO for the compounds remained unchanged while the LUMO decreased from 2.77 eV ($n = 1$) to 3.00 eV ($n = 3$). The best homojunction device was obtained for $n = 1$ with a bluish green maximum luminance of 3300 cd/m^2 and a current efficiency 0.9 cd/A [8].



PQ(OXD)$_n$T, n=1,2,3

Fig. 2 Chemical structure of bipolar small molecules with different number of 1,2,4-oxadiazole units

The third series of bipolar small molecules studied was on the effect of the size of the aromatic moiety. The

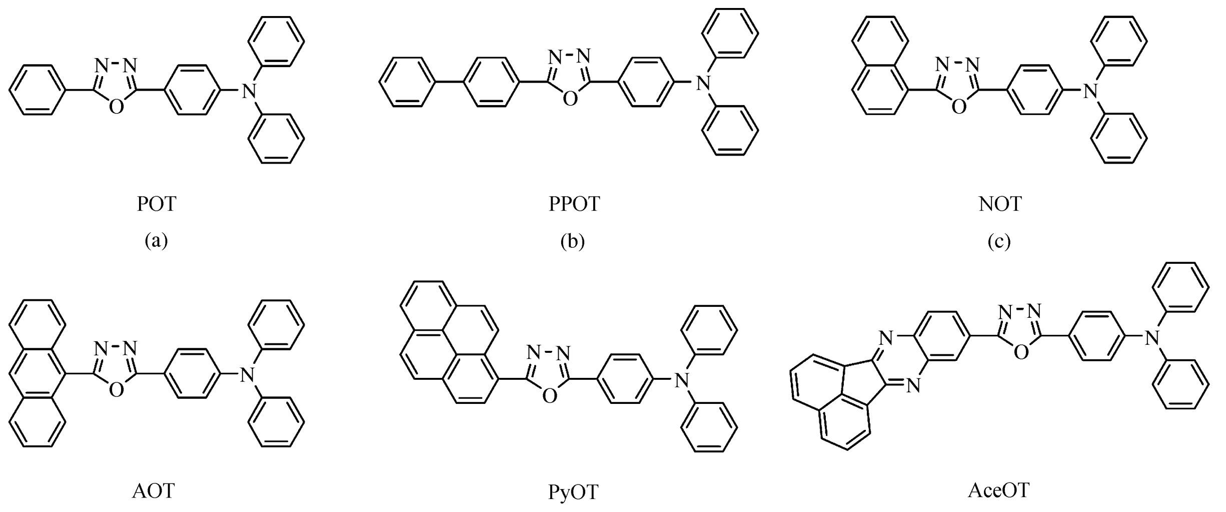


Fig. 3 Chemical structure of bipolar small molecules with different aromatic moieties. (a) POT; (b) PPOT; (c) NOT; (d) AOT; (e) PyOT; (f) AceOT

donor-acceptor type bipolar compounds have the general structure Ar-OXD-T in which Ar represents the polycyclic aromatic moieties including phenyl (POT), biphenyl (PPOT), naphthyl (NOT), anthracenyl (AOT), pyrenyl (PyOT) and acenaphtho[1,2-b]quinoxalinyl (AceOT); OXD represents the electron deficient 1,3,4-oxadiazole, while T is an electron rich diphenylamine (as shown in Fig. 3). The changes in thermal and optical properties for the compounds with Ar were significant. The highest Tg was 139°C for AceOT while the smallest compound POT was mostly crystalline ($T_m = 146°C$). The XOT compounds also covered the full visible spectrum from bluish for POT, PPOT, NOT, greenish for PyOT, yellowish for AOT and reddish for AceOT. Their HOMOs were slightly higher than expected, at 5.46 eV for POT to 5.47 eV for AceOT due to the TPA being rather oxidation reactive compared to TPD, while the LUMO ranged from 2.31 eV for POT to 2.94 eV for AceOT. In general, the CV studies indicated that the XOT compounds were indeed bipolar in nature. We have also attempted to measure the mobility of each of small molecules by the TOF method. It was found that the electron mobility measurement was sensitive to moisture in air and was not obtained for each of the individual compounds. The hole and electron mobility obtained for one of the compound (AOT) is presented in Fig. 4. The results clearly indicated charge balance can be attained. The best homojunction devices were from PyOT with over 7500 cd/m^2 in luminous intensity and 2.2 cd/A in current efficiency.

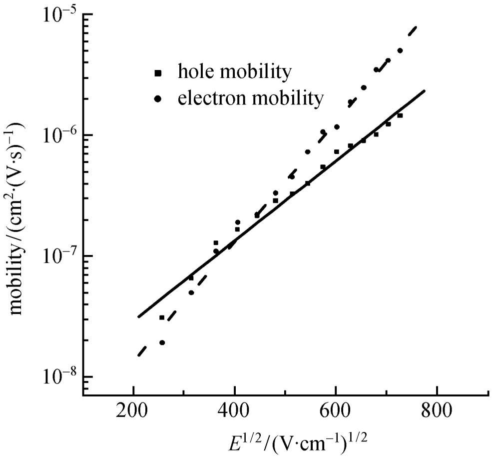


Fig. 4 TOF measurement of hole and electron mobility for bipolar compound AOT (temperature is 289 K)

3.2 Conductive vinyl MeONPA/OXD copolymers for heterojunction OLEDs

Unlike small molecules, polymers usually have higher Tg and can be processed by the lower cost solution method. Conductive vinyl polymers also have better solubility despite their high MW. Due to short range electron delocalization on the side-chain aromatic moiety, they are mostly optically clear compared to main-chain conductive polymers like PPV or polyfluorene. Copolymers with different compositions and therefore different physical/electrical properties can be prepared easily by adjusting the monomer feed ratios in a solution copolymerization reaction. Self-assembly block copolymers that can produce the paracrystalline mesophase can also be obtained by special polymerization methods like ionic copolymerization. Alq$_3$ is a green emitter and a common electron transporting material. Since the mobility for most hole transporting compounds such as TPD and NPB are 1–2 orders higher than Alq$_3$, diffusion of holes into the Alq$_3$

layer produces reactive cationic species which eventually leads to the formation of dark spots in Alq_3-based devices. It is therefore desirable to have a hole transporting layer that can match the electron mobility of Alq_3 in order to produce a charge balance device. A series of copolymers based on MeONPA and OXD with different compositions were prepared by solution copolymerization of the two vinyl monomers at different feed ratios (as shown in Fig. 5) [15]. The final copolymer compositions were determined by ^{1}H-NMR and FT-IR. MeONPA/OXD copolymers were bipolar yet hole-limiting (due to the low lying HOMO for oxadiazole). In an attempt to prepare charge balance heterojunction OLEDs, devices with the configuration ITO/PEDOT/copolymer (100 nm)/Alq_3/Ca/Al were prepared. At an optimum copolymer composition (MeONPA/OXD = 82/18 molar ratio), the maximum luminance and efficiency achieved were over 23000 cd/m^2 and 4.2 cd/A. The emission spectrum was the same for Alq_3. Abrupt change in the current efficiency curve (cd/A vs mA/m^2) at high current density usually associated with the formation of cationic Alq_3 species was not detected for devices employing copolymers with the same or higher OXD contents. The limitation of hole current for the MeONPA/OXD copolymers at high OXD ratios was confirmed by preparing hole-current only devices using high work function gold (−5.1 eV) as the cathode (device configuration: ITO/PEDOT:PSS/copolymer/Au).

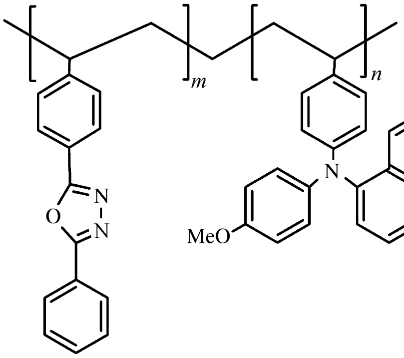


Fig. 5 Chemical structure of conductive vinyl copolymers (poly(MeONPA/OXD)) for charge balance Alq_3-based heterojunction OLED application

3.3 Conductive vinyl MeONPA/OXD copolymers for homojunction OLEDs

The same MeONPA/OXD copolymer series were studied for their application for homojunction OLEDs. The single layer device has the configuration ITO/PEDOT/Copolymer/Ca/Al, in which the bipolar copolymer assumed the multi-roles of hole, electron transportation and emitter as well [9]. In general, it was found that the homojunction devices did not performed well as the bluish MeONPA is not a strong emitter. An orange-red dopant, rubrene, was therefore added to the copolymer from 0.01 wt%–5 wt%. A list of the device performance both for the undoped (S1–S5) and rubrene doped (S6–S9) homojunction PLED devices are given in Table 1. It was shown that the best luminance (current efficiency) increased four-fold from 420 cd/m^2 (0.12 cd/A) to 1484 cd/m^2 (0.74 cd/A) for the copolymer with 69/31 (mol/mol) in MeONPA/OXD composition and 0.1 wt% rubrene doped. At 0.01 wt% rubrene, the EL spectrum (as shown in Fig. 6) exhibited both the NPA emission at 454 nm and rubrene emission at 560 nm. At higher rubrene composition, the NPA emission diminished and full rubrene EL characteristic appeared at 0.1 wt% rubrene and above (as shown in Fig. 7). The guest-host energy transfer can be described as Forster-like as the emission spectrum of the NPA moieties overlapped significantly with the absorption of rubrene. The CIE coordinates (0.348, 0.426) for the device S6 (with 0.01 wt% rubrene) is also presented in Fig. 7, indicating its near white emission.

4 Conclusion

Stability of organic electroluminance devices can be preserved by the balance of charges injected into the individual organic layers. Although heterojunction devices have the highest luminance achieved for OLEDs so far, homojunction devices have the advantages of simple device structure and lower manufacturing cost. It has been demonstrated from the various series of bipolar small molecules studied that the optimum molecular structure for a charge balance homojunction device should contain a large polycyclic aromatic moiety, an electron rich TPD for reversible anodic oxidation. TOF measurement confirmed that charge balance is indeed possible with proper chemistry. In addition, bipolar materials with tunable charge transport properties can also be prepared simply by copolymerization of two or more vinyl monomers with different charge transport properties at a given monomer feed ratio. Other than high Tg, conductive vinyl copolymers can be solution cast despite its high MW. The achievement of charge balance with Alq_3-based heterojunction devices has been demonstrated for the poly(MeONPA/OXD) copolymer series. Color tuning and improved device properties can be achieved simply by doping the homojunction PLEDs. The homojunction PLED was found to achieve improved device performance by the addition of 0.1 wt% rubrene as dopant, while at 0.01 wt% rubrene, a near white color emission was observed.

Acknowledgements This work was supported by a Hong Kong SAR government research grant (No. HKBU2105/06E). The authors would also like to thank the TOF mobility measurement conducted by Prof. S. K. So and Mr. K. L. Tong at the Physics Department of HKBU.

Table 1 Device properties of both undoped (S1–S5) and rubrene doped (S6–S9) homojunctions PLEDs

device structures	$\lambda_{\max}^{\mathrm{EL}}$ (80 mA/cm^2) /nm	FWHM (80 mA/cm^2) /nm	max luminance /(cd·m^{-2})	voltage at max luminance /V	max device efficiency /(cd·A^{-1})	current density at max device efficiency /(mA·cm^{-2})	voltage (25 mA/cm^2) /V
(S1) ITO/PEDOT:PSS/P(MeONPA)/Ca/Al	455	85	232	12.8	0.11	12	8.6
(S2) ITO/PEDOT:PSS /P(MeONPA-co-OXD 69:31)/Ca/Al	460	80	420	15	0.12	239	9.6
(S3) ITO/PEDOT:PSS /P(MeONPA-co-OXD 47:53)/Ca/Al	455	80	336	15.4	0.22	67	11.3
(S4) ITO/PEDOT:PSS /P(MeONPA-co-OXD 26:74)/Ca/Al	458	76	65	21	0.04	133	15
(S5) ITO/PEDOT:PSS/P(OXD)/Ca/Al	n/a	n/a	n/a	n/a	n/a	n/a	17
(S6) ITO/PEDOT:PSS/P(MeONPA-co-OXD 69:31 + 0.01 wt% rubrene)/Ca/Al	456, 550	n/a	532	14	0.18	40	10.1
(S7) ITO/PEDOT:PSS/P(MeONPA-co-OXD 69:31 + 0.1 wt% rubrene)/Ca/Al	456, 550	n/a	1484	17	0.74	45	13.4
(S8) ITO/PEDOT:PSS/P(MeONPA-co-OXD 69:31 + 1.0 wt% rubrene)/Ca/Al	554	67	1260	18.8	0.56	116	14.8
(S9) ITO/PEDOT:PSS/P(MeONPA-co-OXD 69:31 + 5.0 wt% rubrene)/Ca/Al	562	70	232	25	0.1	57	18.1

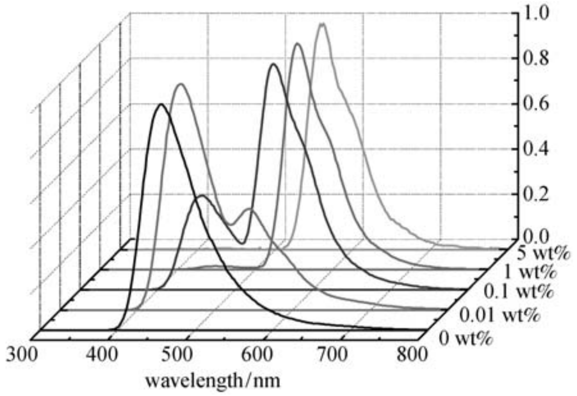


Fig. 6 EL spectrum of rubrene doped homojunction PLEDs

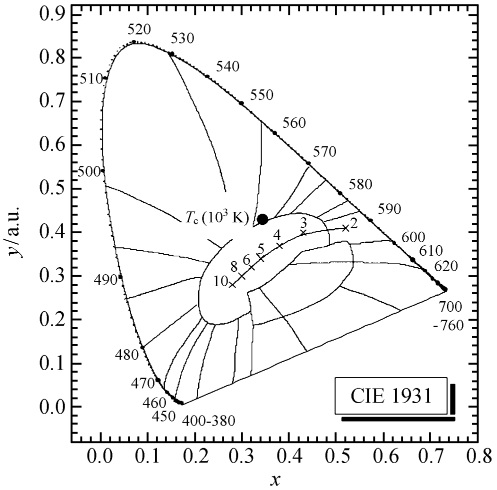


Fig. 7 CIE coordinate for near white device S6 (0.01 wt% rubrene)

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