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Thin-Films of Poly-Triarylamines for Electro-Optic Applications

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Summary

We observed that a new anionic triarylamine copolymer, which is easily accessable by radical polymerization can be used for the preparation of thin semiconducting organic films in two extremely different ways: One is the LBL assembly from solution with a cationic polyelectrolyte as counter system; the other is direct vacuum deposition, whereby the polymer degrades to oligomers, but keeps the functional groups intact as proved by UV/Vis, NMR spectroscopy and cyclic voltammetry. The fabricated films are used in light emitting devices as hole transporting layers showing excellent properties. External EL quantum efficiency (η_{ext}) and luminous efficiency-current density (J) characteristics of PLED device were studied.

Introduction

Organic semiconductors and conjugated polymers are currently of wide interest for applications in electronic and optoelectronic devices including light-emitting diodes [1-5], thin film transistors [6-10], photovoltaic cells [11-14] and electrochromic device [15,16]. Semiconducting polymers have the advantage of allowing an easy, low-cost manufacture of large-area displays using solution-processing of film-forming polymers. In particular, polymer light emitting diodes (LEDs) show attractive device characteristics, involving efficient light generation, and several development programs are set-up to establish procedures for manufacture. The triarylamine moiety –mostly in polymeric form- is the most widely used hole-transporting material due to the electron-donating nature of the nitrogen atom in LEDs [17,18]. Under the influence of an electric field, the positive charge is transported by a hopping mechanism and drift mobilities up to 10^{-3} cm^2/ (V•s) are possible [19]. Due to the high charge carrier mobility of triarylamine polymers, they can be effectively used in LEDs as hole transporting materials.

Usually polymer thin films are prepared from organic materials in solution by solution-dipping or spin-coating method onto transparent conductive oxide (TCO)-coated glasses. Although good results were achieved this way, there are a number of problems that can arise. It can be difficult to find suitable solvents to prepare thin films (50-400 nm) that are free from pinholes. Moreover, if there are suitable solvents without any pinholes on the surface, mutually exclusive solvents for the different polymer layers in a multilayer device are also difficult to engineer. As a next problem, oxygen and other contaminants (e.g., dust) are difficult to exclude from the solutions used to make films and solvent not fully removed from the films after deposition. They can cause formation of voids and chemical reactivity with the electrodes and finally minimize device performance. At that point, dry processes such as vapor deposition under vacuum condition can be the perfect candidates to deposit the polymer films for LEDs. Vapor deposition method provides a clean environment; it is solvent free and well suited to sequential depositions in hetero-structured multilayer system. Moreover, the device fabrication by the vacuum deposition method allows a whole processing in the same run without vacuum breaking from the polymer materials to the metal upper electrode. Vapor deposition method has been explored for sublimation of low-molecular-weight dyes [20], oligomers [21,22] but only a very limited number of polymers. That is, because polymers generally cannot be vaporized. On the other hand: many polymers decompose to oligomers at elevated temperatures [23-25]. Thus polymers may act as precursors for oligomers, which can be vaporized. Such evaporated oligomers could benefit from the advantages described above and they may give more stable amorphous structures–compared to low molar mass materials.

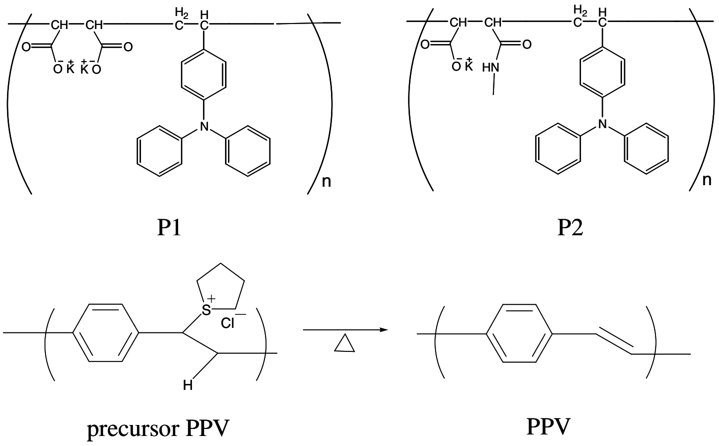
We found now that a triarylamine polymer, which we made intentionally for the layer-by-layer (LBL) assembly can also be vaporized. Thus this polymer can enter the processing scheme for the preparation of organic LEDs in two ways: by solution processing and by evaporation. During the evaporation process, this polymer undergoes imidization at elevated temperature, afterwards, giving rise to high quality films for LEDs.

Results and Discussion

As hole transporting functional moiety, the p-type triarylamine polymers were synthesized using the synthetic route described elsewhere [26] (see Experimental Part). The chemical structures of the polymers are shown in Scheme 1.

Due to their negative charges, the synthesized polymers **P1-P2** are suitable for deposition by the LBL method from solution using spin coating technique with oppositely charged cationic precursor poly (phenylenevinylene) (PPV). Since the first report of Decher and coworkers in the early 1990s, there have been numerous reports on the LBL assembly based on the electrostatic attraction between polycations and polyanions [27]. The LBL technique can form a variety of ultra-thin interfacial layers and create films comprised of semi-interpenetrated bilayers of polycations and polyanions. Moreover, the film thickness can be easily controlled at the molecular level and a multilayer architecture does indeed make it possible to realize significant improvements in the device performance [28].

The optical properties of **P1** and **P2** were investigated by UV/Vis and photoluminescence (PL) spectroscopy, as thin mono-layer films assembled on quartz



Scheme 1. Triarylamine polymers **P1-P2** and precursor PPV.

substrates by spin-coating method. The electrochemical properties of the **P1-P2** were evaluated using cyclic voltammetry (CV) using a three-electrode cell. Upon oxidation of the films the oxidation peak (E_{ox}) of **P1** appears at 871 mV and the oxidation peak of **P2** appears at 847 mV. These values are characteristics for triarylamine moieties in polymers. As the potential gets reversed from +1.6 V to 0 V, two reversible reduction waves (E_{red}') can be observed for two polymers identically. The first peak at about 760 mV corresponds to the reduction of the triarylamine radical-cation. The second peak at 646 or 634 mV can be attributed to the reduction of the oxidized dimer, formed from the radical-cations during the first oxidation cycle. Generally unsubstituted triarylamines undergo dimerization and the resulting dimers show both a reduced oxidation potential and an increased charge carrier mobility [29]. In addition, the formation of the dimer is the key factor to achieve stable films, both with respect to mechanical stability (no dissolution due to the crosslinking) and chemical stability (more stable radical cations of the dimer, see Ref. 26 for comparison). Concerning the use of hole transporting materials in devices, optimized energy band gap (E_g) of the polymers, which are defined with both the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital) levels, are necessary. Based on the optical and electrochemical data, the energy levels can be calculated. All values are listed in Table 1.

Table 1. Optical and electrochemical properties and energy levels of the **P1** and **P2**.

Polymers	UV/vis λ_{max} solution (nm)	UV/vis λ_{max} film (nm)	$E_g{}^a$ (eV)	PL λ_{max} solution (nm)	PL λ_{max} film (nm)	E_{ox} (mV)	E_{red}' (mV)	HOMO^b (eV)	LUMO^c (eV)
P1	299	308	3.04	455	462	871	753, 646	5.27	2.23
P2	301	305	3.03	460	460	847	760, 634	5.25	2.22

[a] Band gaps were calculated from the onset of the UV/Vis absorption spectra.

[b] HOMO levels were converted from the measured oxidation potentials assuming the absolute energy level of ferrocene to be -4.8 eV [29].

[c] LUMO levels were estimated from the HOMO levels and energy gaps.

Thin film LEDs based on multi-bilayer combinations of the conjugated poly (phenylene vinylene) (PPV) and different polyanions have been fabricated via the use of the LBL molecular-level processing scheme [30,31].We used that concept to prepare multilayer thin films (spin-coating variant of LBL) from combinations of **P1** and **P2** and the precursor of PPV (Scheme 1). Multilayers, which grow constantly in thickness, could be obtained (see Ref. 32 for comparison). To investigate the electroactivity of the multilayer film the multilayer build-up was also performed on ITO-coated glass substrate, on which alternatively 20 or 40 bilayers of **P1** or **P2** and precursor PPV polycation solutions were deposited by the spin-coating variant of LBL. The thermal conversion of the PPV precursor to the conjugated form of PPV was done by heating the (**P1-P2/**precursor PPV)n films from room temperature to 180°C, holding at that temperature for 10 h, and then allowing the samples to cool back down to room temperature over a 4 h period, all under vacuum.

We have fabricated simple PLED device with the configuration of ITO/(**P1-P2/**PPV)n films/LiF/Al. Figure 1 shows the light intensity-voltage plots and relative device efficiencies of PLEDs. The turn-on voltages of the (**P1/**PPV)20 and (**P2/**PPV)20 devices were found to be about 2.8 V and 2.2 V. The thicker (**P1/**PPV)40 and (**P2/**PPV)40 devices show about 6.4 V and 3.8 V as the turn-on voltage. Interestingly, the (**P1-P2/**PPV)40 device shows dramatically increased turn-on voltage compared to the (**P1-P2/**PPV)20 device. We believe that this thickness dependent behavior can be explained -besides the usual thickness dependence due to constant field strength- by a thickness dependent conversion of the PPV precursor, which gets more limited with increasing thickness. In Figure 1b the light intensity characteristics of **P1-P2/**PPV films with 20-40 bilayers sharply dropped above 80 mA/cm2.

Generally the LED characteristics of theses multilayers is acceptable, but it is definitely poorer, especially with regard to the maximum light density, than plain spin-coated PPV bulk films on ITO substrates [33] In order to improve the device characteristics we used different conversion temperatures for the PPV precursor. Thereby we found by accident that **P2** can be vaporized and vacuum deposited at higher temperatures. Heating **P2** to temperature slightly above 300°C leads to a vaporization of **P2** and a constant growth of an organic film on the substrate. This material will be called **P2 vap**. in the following.

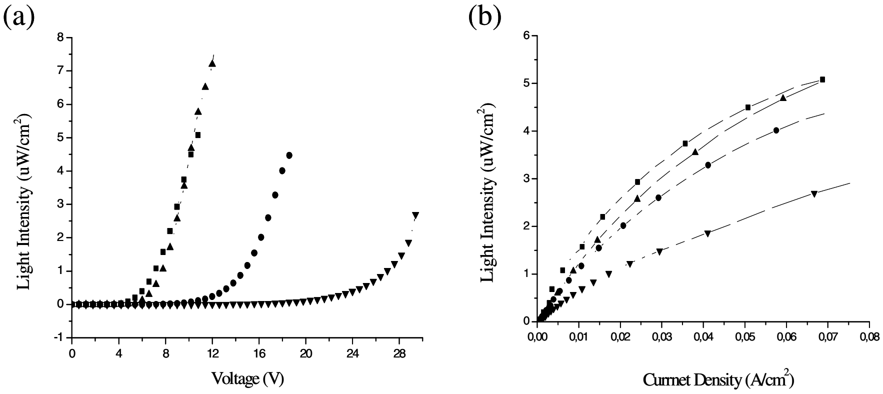


Figure 1. Light intensity-voltage plots and relative device efficiencies obtained from light emitting devices of ITO(**P1-P2/**PPV)n/LiF/Al. Symbol represents the number of **P1-P2/**PPV bilayers: (■) (**P2/**PPV)20 , (▲) (**P1/**PPV)20 , (●) (**P2/**PPV)40 and (▼) (**P1/**PPV)40.

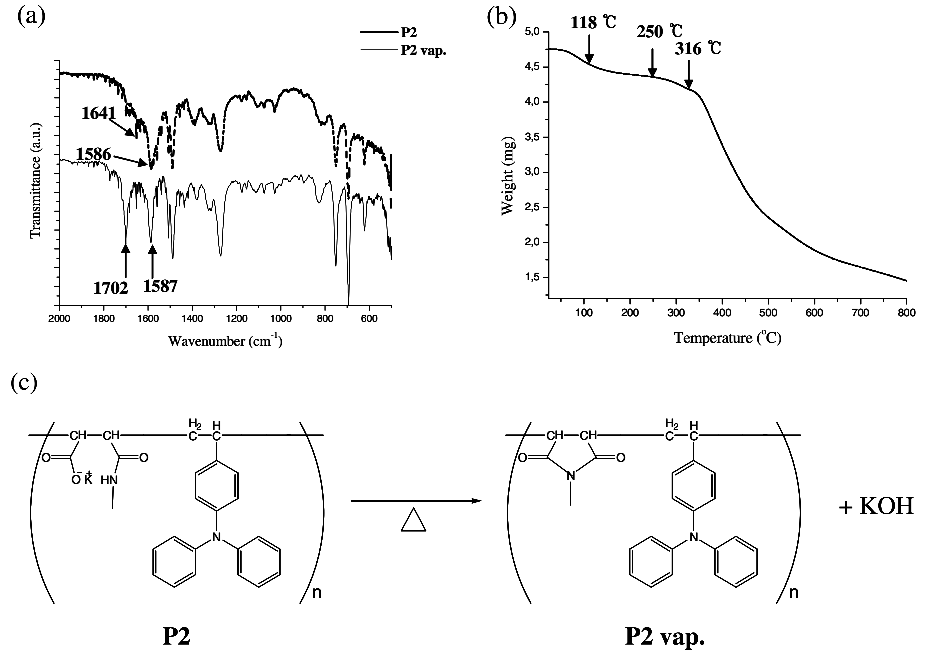


Figure 2. (a) The IR spectra of **P2** before and after (**P2 vap.**) vacuum deposition process (b) TGA thermogram of **P2**. (c) The estimated secondary reaction of **P2**.

Although very little amount of evaporated material was available, we succeeded in analyzing the organic film of **P2** vap. formed on the substrate by cyclic voltametry and UV, ^{1}H NMR and FT-IR spectroscopy. ^{1}H NMR shows that in the deposited material all functional groups are still present: the triarylamine (7.23~7.02 ppm in CD_2Cl_2), as well as the methyl group on the nitrogen of the comonomer (1.66 ppm in CD_2Cl_2, see Experimental section). UV spectroscopy and CV show that the position of HOMO and LUMO levels is unchanged. FT-IR measurements showed, however, a difference before and after vacuum deposition (see Figure 2a). For the parent polymer **P2**, a sharp carboxylate peak at 1586 cm^{-1} and a weak amide peak at 1641 cm^{-1} were observed. After vacuum deposition (**P2 vap.**), the amide peak has disappeared and it is replaced by a strong new peak at 1702 cm^{-1}, which can be assigned to the imide bond. Such a reaction is not unexpected since imidization (Figure 2 (c)) of amide – acid at higher temperatures is a classical reaction [33,34]. Imidization explains also the difference between **P1** and **P2** during heating. **P1**, which has two carboxylate groups at the comonomer unit, cannot form an imide. As a result, it stays a highly charged polymer, of which fragments can hardly vaporize. **P2**, on the contrary, looses –at least most of- its ionic character during imidization and fragments can more easily vaporize.

To study the chemical processes during the heat treatment of **P2** thermo-gravimetric (TGA) measurements was carried out under dried nitrogen gas. Figure 2(b) shows the three-step weight loss as result. The first step appears below 118°C and involves a small weight loss. It can be attributed to the evaporation of DMF and H_2O used as solvents during synthesis and purification. The second step occurs over the range 118 ~ 250°C and involves also relatively small weight loss. This small weight loss is

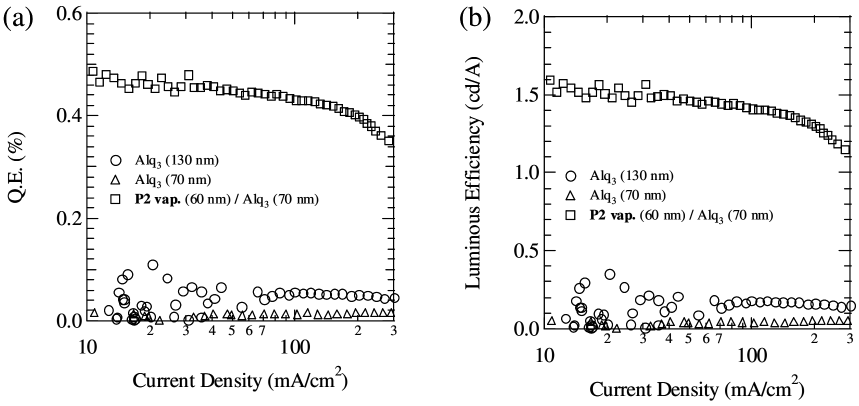


Figure 3. (a) The external EL quantum efficiency (η_{ext}) -current density (J) characteristics (b) luminous efficiency-current density (J) characteristics of PLEDs using vacuum deposited **P2 vap.** film as hole transporting layers.

most likely due to traces of water formed as a byproduct of the imide-ring. Although imidization is the major reaction it cannot lead to a large weight loss, because mostly KOH is formed during the reaction of potassium carboxylate with the amide group. When the temperature is raised above 320°C the most significant weight loss occurs. It is due to the degradation of the imidized polymer chains. From the TGA results, we conclude that in the heating run, the **P2** is partially degraded at above 320°C and it leads to oligomeric structure with all subunits in tact. This assumption is in agreement with UV- and ^{1}H-NMR spectroscopy and the GPC-measurements of the evaporated material. For the deposited oligomers of **P2 vap.**, an M_w of 2100 is found, which is much smaller than the M_w of the parent **P2** (151 000, see Experimental Part).

Since oligomeric **P2 vap.** can act as hole transporter, we have fabricated simple LED devices with the configuration of ITO / vacuum deposited **P2 vap.** film / Alq$_3$ / LiF / Al. Thus the film does not contain PPV and Alq$_3$ acts as emitter. Figure 3(a) and 3(b) show the external EL quantum efficiency (η_{ext}) and the luminous efficiency-current density (J) characteristics of LEDs using vacuum deposited **P2 vap.** film as hole transporting layer. A maximum η_{ext} of 0.48 % was obtained at a current density of J = 31 mA/cm^2 and a maximum luminous efficiency of 1.6 cd/A was found at same current density. The insertion of the **P2 vap.** as hole transport layer in between ITO and Alq$_3$ increases the quantum efficiency (QE) and luminous efficiency. These values are rather good for such films and especially the quantum efficiency is highly improved compared to the films presented in Figure 1. This demonstrates the potential of the vacuum deposited films. We assume that the good performance of the vacuum deposited films is due to the fact that the film is very homogenous and especially free of ions.

Conclusions

We observed that some anionic polymers with triarylamine moieties, which are easily accessible by radical polymerization, can be used for the preparation of thin semiconducting organic films in two extremely different ways: One is the LBL assembly from solution with a cationic polyelectrolyte as counter system; the other is direct vacuum deposition, whereby the polymer loses its ionic character (imidization) and degrades to oligomers, while keeping the functional groups intact. The layer build-up by LBL with precursor PPV as polycation allows, thereby, fine tuning of the film thickness (number of deposition cycles) and the preparation of organic LEDs. The vacuum deposition of oligomers (**P2 vap.**) has the advantage that a multilayer LED can be produced without vacuum breaking.

A direct comparison of the organic LEDs prepared with both methods is difficult, because different layer structures were prepared. By LBL assembly (spin-coating variant) layers intermixed at a –more or less- molecular level from polytriarylamine (hole conductor) and PPV (emitter) were prepared. This film can be used as LED, but its performance was poorer as that of LEDs [33] from plain spin-coated PPV bulk films deposited at ITO. Vacuum deposition of oligomers was used to build a two-layer structure with the triarylamine oligomer for hole transport and Alq_3 as emitter. This set-up gave a very nice LED, with highly improved quantum efficiency. We assume that its good performance results from the fact that this film is free of ions.

Experimental Section

^1H NMR spectra were measured on a Bruker 300 MHz FT spectrometer. Infrared spectra were measured on a Bruker Vector 22 FT-IR spectrometer with a Harrick ATR unit. Gel permeation chromatography (GPC) at RT was used to determine the molecular weight with THF as eluent. For this purpose combination of a Jasco PU-1580 pump, Autosampler AS 1555, UV-detector UV 1575 and RI-detector RI 1530 were used. (Wyatt light scattering, MZ-Gel SDplus10^2, 10^4 Å and 10^6 Å). To evaluate the data universal calibration based on polystyrene standards was used. UV/Vis absorption spectra were taken with a Shimadzu UV-2102 PC spectrometer and photoluminescence (PL) spectra were taken with a Fluoromax-II fluorometer (ISA). All electrochemical tests were performed using an Autolab PGSTAT30 (Eco Chemie) Potentiostat/Galvanostat. Pt wire and Ag/AgCl were used as the counter and reference electrodes. Polymer films coated on ITO-coated glass were used as the working electrodes and 0.1 M tetrabutylammonium tetrafluoroborate ($TBABF_4$) in acetonitrile was used as the electrolyte using ferrocene as the internal standard. For these investigations, thin mono-layer **P1-P2** films were coated on Pt-working electrodes from the polymer solution in THF:H2O = 5:1 mixture solvents [26]. The scan for cyclic voltammograms of **P1** and **P2** was made anodically, proceeding from 0 V to +1.1 V. The substrates were treated by UV ozone ambient condition of a UVO cleaner, UVO-42 and for spin-coating; a Convac ST146 spin-coater was used.

Preparation of triarylamine polymer P1-P2 and their multilayer build-up

The synthesis of the polymers started with the radical copolymerization of maleic anhydride and triarylamine monomers and the multilayer build-up of polymers **P1-P2** is described elsewhere [26] in more detail. To determine the molecular weight, the resulting alternating copolymer was analyzed by GPC with THF as eluent; a M_n : 98720 g/mol , M_w : 150900 g/mol and polydispersity index (PDI) (M_w/M_n) : 1.53 were found. After treatment of the potassium hydroxide or alkyl amine solution, the synthesized polymers **P1** and **P2** are composed with two different moieties; one part is the two carboxylate groups derived from maleic anhydride for **P1** or only one carboxylate group and amide group derived from maleic anhydride and amine solution for **P2** and the other part is triarylamine.

P1: ^{1}H NMR (CD_2Cl_2, 300 MHz): $\delta = 6.97$ (14H, arom H), 1.66 (5H, main chain)
IR (ATR): 1586 (CO) cm^{-1}

P2: ^{1}H NMR (CD_2Cl_2, 300 MHz): $\delta = 6.93$ (14H, arom H), 2.47 (5H, main chain), 1.82 (3H, NH-$\underline{CH_3}$)
IR (ATR): 1641 cm^{-1} (amide bond), 1585 (CO) cm^{-1}

P2 vap.: ^{1}H NMR (CD_2Cl_2, 300 MHz): $\delta = 7.23$ (4H, arom H), 7.02 (10H, arom H), 2.93 (5H, main chain), 1.54 (3H, N-$\underline{CH_3}$)
IR (ATR): 1702 cm^{-1} (imide bond), 1587 (CO) cm^{-1}
M_n: 1448 g/mol, M_w: 2079 g/mol, PDI (M_w/M_n): 1.43

The multilayers were build-up by the spin-coating variant of LBL as described in refs. 26 and 32.

The Optical and electrochemical properties and energy levels of the **P1** and **P2** in Table 1 were obtained based on the UV/Vis and PL spectra and CV data. The HOMO and LUMO levels calculated according to an empirical formula, $E_{HOMO} = -e\ (E_{ox} + 4.4)$ (eV) and $E_{LUMO} = -e\ (E_{red} + 4.4)$ (eV) [29]. Band gaps were calculated from the onset of the UV/Vis absorption spectra ($\lambda = 1240$ /V).

P2 vap. film fabrication by vacuum deposition method.

The devices with **P2 vap.** film as the hole-transporting layer (HTL), Alq_3 as the electron-transport layer (ETL) and the cathode of LiF/Al were fabricated on precleaned ITO glass substrates (sheet resistance of about 10 Ω/cm^2). The ITO substrate (10 Ω/cm^2, 150 nm thick) was cleaned ultrasonically in organic solvents (isopropyl alcohol, acetone, and methanol) and rinsed in de-ionized (DI) water. It was dried in an oven kept at 100 ℃ for more than 30 min. The device was fabricated with the successive vacuum deposition of **P2**, Alq_3, LiF, and aluminum (Al), under a vacuum ($< 3 \times 10^{-6}$ Torr) without breaking vacuum. The deposition rates for organic layers were about 0.1~0.15 nm/sec and about 0.3nm/sec for Al. The active area of the OLED, defined by the overlap of the ITO and the Al cathode, was 1.96 mm^2. High conducting PEDOT:PSS (Baytron P AI 4083) was spin-coated (4000 rpm) with thickness 40 nm after passing a 0.5 µm filter. And then dried at vacuum oven in 120°C over 30 min. The current-voltage-luminance (I-V-L) characteristics were measured with a Keithley 236 source-measure unit and a Keithley 2000 multimeter equipped with a PMT through an ARC 275 monochromator. The luminous efficiency was estimated by measuring the EL emission intensity with the calibrated Si photodiode placed at the normal angle to the device surface and assuming that the device is a Lambertian source.

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