



# Sequestration of electroactive materials in a high $T_g$ , insulating polymer matrix for optoelectronic applications. Part 1. Light emitting diode devices

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## Abstract

The use of a high  $T_g$ , insulating polymer to sequester low molecular weight electroactive materials at high addition levels for utility in LED devices has been demonstrated. The threshold for effective light emission appears to be in the range of 15 wt% electroactive compounds in agreement with the percolation theory of deGennes. The high  $T_g$  polymer allows for suppression or elimination of the undesired crystallization of the electroactive species and yields a significant increase in the  $T_g$  of the light emitting layer (also required). Additionally this approach offers the potential for easier (and lower cost) fabrication routes not generally employed for low molecular weight electroactive materials (e.g. spin coating, ink jet printing, roll-to-roll printing). The improved mechanical properties of the light emitting layer with high molecular weight polymer addition should allow for improved performance/durability in flexible displays. The simple blend approach should be an attractive alternative to other more common methods reported in the literature employing covalent bonding of electroactive species to polymeric backbones to achieve the same results. This approach also allows for multiple addition of dopants (e.g. laser dyes), hole transport materials and electron transport materials in a single light emitting layer. While these results demonstrate the concept, optimization was not conducted and significant improvements would be expected with proper adjustment of the many variables possible with this approach.

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*Keywords:* Light emitting diodes; High  $T_g$  polymer; Optoelectronic applications

## 1. Introduction

The discovery of organic/organo-metallic electroactive compounds utility in light emitting diodes (LEDs) [1–3] followed by the observation of  $\pi$ -conjugated polymers offering similar potential [4–8] has resulted in significant academic interest and emerging commercial interest. The intense investigations, which followed have greatly advanced the technology and commercial devices are beginning to emerge. Both small molecule organic light emitting diodes (SMOLEDs or OLEDs) and polymeric light emitting diodes (PLEDs) have common features in device construction and both offer advantages and disadvantages. As the technology continues to advance, higher performance and lower cost will drive this technology into larger markets from flat screen displays to lighting applications and eventually to even low-cost, flexible and disposable displays. Similarities exist in photovoltaic (PV)

devices where both small organic/organo-metallic molecules and conjugated polymers have demonstrated potential also resulting in significant research. Advantages of the small organic molecules include the large number of structures offering electroactive properties, the ability to obtain highly pure monodisperse substances, and well-established deposition techniques for achieving film thickness control. Polymeric materials offer the advantages of higher glass transition temperatures, generally amorphous structures, the ability to be fabricated using less costly approaches, and better mechanical properties for flexible displays. This study evaluates the concept of using a high  $T_g$  polymer matrix to sequester large amounts of small molecule organic electroactive materials for light emitting layers in LED devices. A companion paper will discuss the evaluation of this concept in PV devices. Low molecular weight electroactive compounds are often highly crystalline and thus not adequate for LEDs as amorphous materials are generally required. Even the amorphous compounds often have glass transition temperatures too low for device use as amorphous glasses are required with  $T_g$ s well above operating or exposure temperatures (generally 75 °C or higher). Many low molecular weight electroactive species either have poor stability or vapor

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pressure too low for typical vacuum deposition conditions. Additionally, low molecular weight amorphous glasses have very poor mechanical properties and cannot be employed in flexible displays. Lower cost manufacturing processes proposed for flexible displays such as ink jet printing, screen printing, roll-to-roll printing, generally cannot be considered for the low molecular weight compounds. Various approaches have been discussed in the literature to resolve these problems often involving covalent bonding of the electroactive species to non-active polymer backbones. Miscible blends of these compounds sequestered in a high  $T_g$  polymer matrix could solve many of these issues if the performance characteristics they offer for LED devices can be maintained. This study was conducted to demonstrate the concept and investigate several of the variables involved with LED fabrication and evaluation.

The combination of electroactive organic compounds in non-electroactive polymer blends has been investigated in a few prior studies including the addition of DCM laser dye and substituted phenylenevinylene oligomers to polystyrene [9]. These compounds added up to 20 wt% showed interesting  $I$ – $V$  (current–voltage) results above 15 wt% of a substituted phenylenevinylene oligomer indicating the onset of percolation. This threshold is similar to that predicted by the deGennes percolation theory [10] for heterogeneous mixtures and thus appears to be valid for molecularly miscible systems at least in this example. PMMA containing 50 wt% TPD (*N,N*-diphenyl-*N,N*-di(*m*-tolyl)-*p*-benzidine) and  $\text{Alq}_3$ (tris(8-quinolinolato)aluminum) (TPD/ $\text{Alq}_3$  ratio from 0.43 to 1) was evaluated in an LED device offering brightness of 920  $\text{cd}/\text{m}^2$  at 17 V [11]. Blends of TPD in a poly(aryl ether ketone) ( $T_g = 252$  °C) and a poly(imidoaryl ether sulfone) ( $T_g = 323$  °C) were investigated as a hole transport layer for a LED device where  $\text{Alq}_3$  was employed as the light emitting layer [12]. It was noted that TPD has a low  $T_g$  of 60 °C and while amorphous layers can be obtained from vacuum deposition it has a tendency to crystallize upon aging and modest temperature exposure. The sequestration in the high  $T_g$  polymers prevented crystallization and allowed for improved morphological stability. A LED device based on PPV (poly(phenylene vinylene) made from a soluble precursor) as the hole transporting layer and a light emitting layer of a PPV segmented block copolymer (3 wt%) blended into poly(*N*-vinyl carbazole) employed a blend of butyl-PBD(2-(4-biphenyl)-5-(*t*-butylphenyl)-1,3,4-oxadiazole)/PMMA 3/1 by wt as the electron transport layer [13]. MEH-PPV blends with PMMA were investigated in light emitting devices to study the morphology [14]. At low MEH-PPV levels, isolated light emitting domains with diameters of 300–900 nm with 100 nm thickness were observed. A patent notes the use of polymeric binders for low molecular weight hole transport materials for the hole transport layer of LED devices with examples including polysulfone and tertiary aromatic amines [15]. The utility of a high  $T_g$  insulating polymer to sequester low molecular weight electroactive compounds for the light emitting layer in LED devices appears to be novel as disclosed in a recent patent [16] and initially published in a condensed form in a conference proceedings

[17]. Specific data and figures from Ref. [15] have been included (with permission) in this paper.

Conjugated or other electroactive polymers are often modified with low molecular weight electroactive compounds to improve efficiency or tune the emission spectra. An early study reported by Partridge [18] noted electroluminescence emission from poly(*N*-vinyl carbazole) containing electron-accepting compounds such as cyano-substituted benzene. Poly(*N*-vinyl carbazole), a hole transport polymer, doped with 2-(4-biphenyl)-5-(*t*-butylphenyl)-1,3,4-oxadiazole and emitter molecules such as Coumarin 6 was employed in a single layer LED device [19]. The light emission was shown to be capable of being modified across the visible spectrum by proper choice of the emitter. Coumarin 515 was employed in poly(*N*-vinyl carbazole) blends in a single layer LED device showing increased external quantum efficiency and appearing to offer better performance than would be achieved with an additional hole-blocking layer [20]. The incorporation of a low molecular weight dye (MPD) into a thiophene vinylene based block copolymer with oligomethylene spacer units provided a bright red emission [21]. The efficient energy transfer between the conjugated copolymer matrix and the dye was attributed to the strength of the emission. Low molecular weight electroactive compounds can also be covalently bonded to non-electroactive polymer backbones offering the potential to be employed in simpler fabrication processes. An example of this involved a copolymer (olefin backbone) with carbazole and oxadiazole side groups [22,23]. The advantages of higher  $T_g$ , elimination of crystallization and easier fabrication were noted for this approach.

Additionally the combination of hole transport and electron transport materials in the same molecule offers the potential for improving device efficiency. The blend approach noted in this paper offers basically the same advantages without the requirement of copolymerization.

A generalized OLED structure is shown in Fig. 1(a). Normally the anode is a transparent conductor such as indium tin oxide (ITO) coated on glass or plastic substrate. The anode injects hole current into the organic layer. On the anode is the hole injection layer (HIL) which provides energy level matching with the work function of the anode, and performs a better hole injection into the hole transport layer (HTL) than the anode. The electron injection layer (EIL) and electron transport layer (ETL) is similar to HIL and HTL, respectively, except that they are related to electron related functions and energy level matching is relative to the work function of the cathode. The light emitting layer in the middle of the device is where light originates from. When making display or lighting devices, at least one of the electrodes (the anode and the cathode) is transparent. Since the device is sensitive to moisture/oxygen, the device is normally hermetically encapsulated for different applications. The encapsulation layer is not shown in Fig. 1(a). In real display, each pixel will have an OLED. In color (RGB) display, each pixel has three subpixels, i.e. red, green and blue subpixels.

The multilayer device configuration offers the advantage of being able to optimize the properties of the materials used

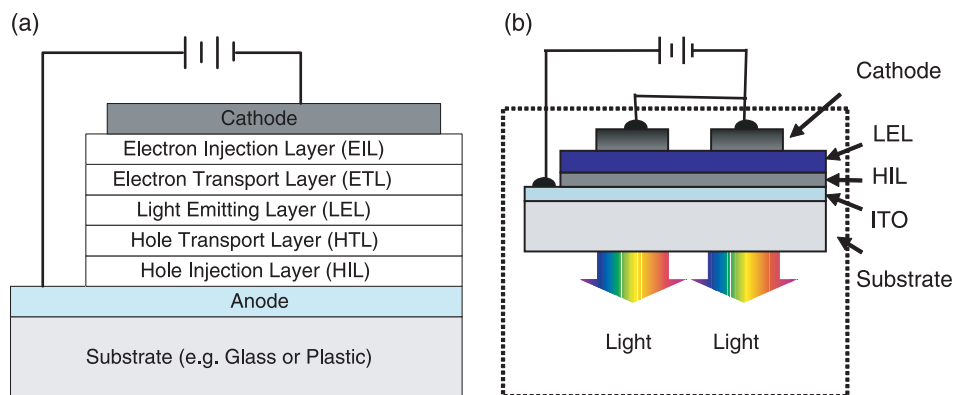


Fig. 1. OLED device configurations. (a) a multilayer device configuration; (b) a double layer device configuration.

for each layer, and adjust the layer thickness according to the property of the materials to balance the hole and electron injection into the light emitting layer and improve device efficiency. However, the manufacturing cost also increases with the number of layers used in the devices. Since low manufacturing cost is critical for commercial applications, and single layer device normally does not have the required performance, the double layer device structure is a commonly used trade-off between cost and performance [24], as shown in Fig. 1(b). In a double layer device, each layer has multiple functions, e.g. charge injection/transport or charge transport/emission. This is especially true for PLED. Since this paper is focused on mainly PLED, most of the devices used have the double-layer configuration shown in Fig. 1(b). For SMOLED, so far the devices typically employ more than two layers for optimized performance.

When evaluating the performance of OLED devices, the figures-of-merit are (1) turn-on voltage ( $V_{on}$ ) and operation voltage—the lower, the better.  $V_{on}$  is normally considered as the voltage at which the device starts to emit light. However, the definition of ‘emit light’ is not universal. It is sometimes defined as the onset of visual detection or when the voltage yields a specific level of brightness (often 1 or 5  $\text{cd}/\text{m}^2$ ); (2) quantum efficiency ( $\eta$ ), defined as the number of photons emitted per electron injected. The higher the  $\eta$ , the better the device; (3) power efficiency, defined as the ratio of emitted optical power to injected electrical power. In the PLED industry, current efficiency is generally employed, which is defined as the ratio of brightness to current density, in unit of  $\text{cd}/\text{A}$ . (4) Brightness in unit of  $\text{cd}/\text{m}^2$ , the higher the better; (5) leakage current, normally considered as the current passing through the device when the device is not on, for example, when the device is biased reversely or at a voltage lower than the turn on voltage. The lower the leakage current, the better the device. (6) Stability or lifetime of the device. Normally the device lifetime is defined as the time it takes for the device brightness to decrease to half of the initial brightness. So lifetime is brightness dependent. It is frequently cited that for high end commercial applications, a lifetime of 10,000 h is required at a specified brightness for the particular application. It is also important to look at the change of efficiency vs.

voltage (or current density, brightness). A constant efficiency is ideal.

In order to demonstrate the concept of employing a high  $T_g$ , insulating polymer to sequester electroactive compounds, the condensation polymer from 4,4'-dibromobiphenyl to 9,9-bis(4-hydroxyphenyl)fluorene produced by the Ullman reaction was chosen [25]. This polymer, termed PAE-2, has a  $T_g$  of 265 °C, good solvent solubility and exhibits a broad range of miscibility with low molecular weight electroactive compounds. Poly(trimethyl silyl propyne) (PTMSP) was also evaluated in this concept as it exhibits the highest free volume of known polymers [26] and thus has the capability to sequester large molecules without a significant loss in properties. Although PTMSP has alternating double bonds, it is a non-electroactive, insulating polymer.

The chemical structures of the materials used in this study are shown in Fig. 2.

## 2. Experimental

PL spectra were measured using an InstaSpec IV CCD camera from oriel instruments. A 150 W ozone free xenon lamp from Oriel Instruments was used as the excitation light source. The light emitting devices were fabricated on ITO substrates with a sheet resistance of  $\sim 12 \Omega/\lambda$  (from Colorado Coating Concept). The ITO substrates were first ultrasonicated sequentially in DI water with detergent, methanol, isopropanol and acetone. The substrates were further cleaned with oxygen plasma in an SPI Desktop II oxygen plasma etcher for 10 min. For hole injection or transport layer, Baytron® P A14083 poly(ethylene-3,4-dioxythiophene): poly(styrene sulfonic acid) (PEDOT, from Starck) was spin coated at a spin rate of 3000 rpm and annealed at 160 °C for 30 min on a hot plate under a nitrogen atmosphere. The PEDOT:PSSA dispersion was filtered with a 0.45 micron PVDF filter before spin coating. The light emitting layers were spin coated from chlorobenzene solutions of PAE-2 or PTMSP with electroactive molecules and dopants at desired ratios. The concentrations of the solutions range from 10 to 18 mg/mL and the spin rates range from 1000 to 2500 rpm. The samples were then masked for cathode deposition. In the

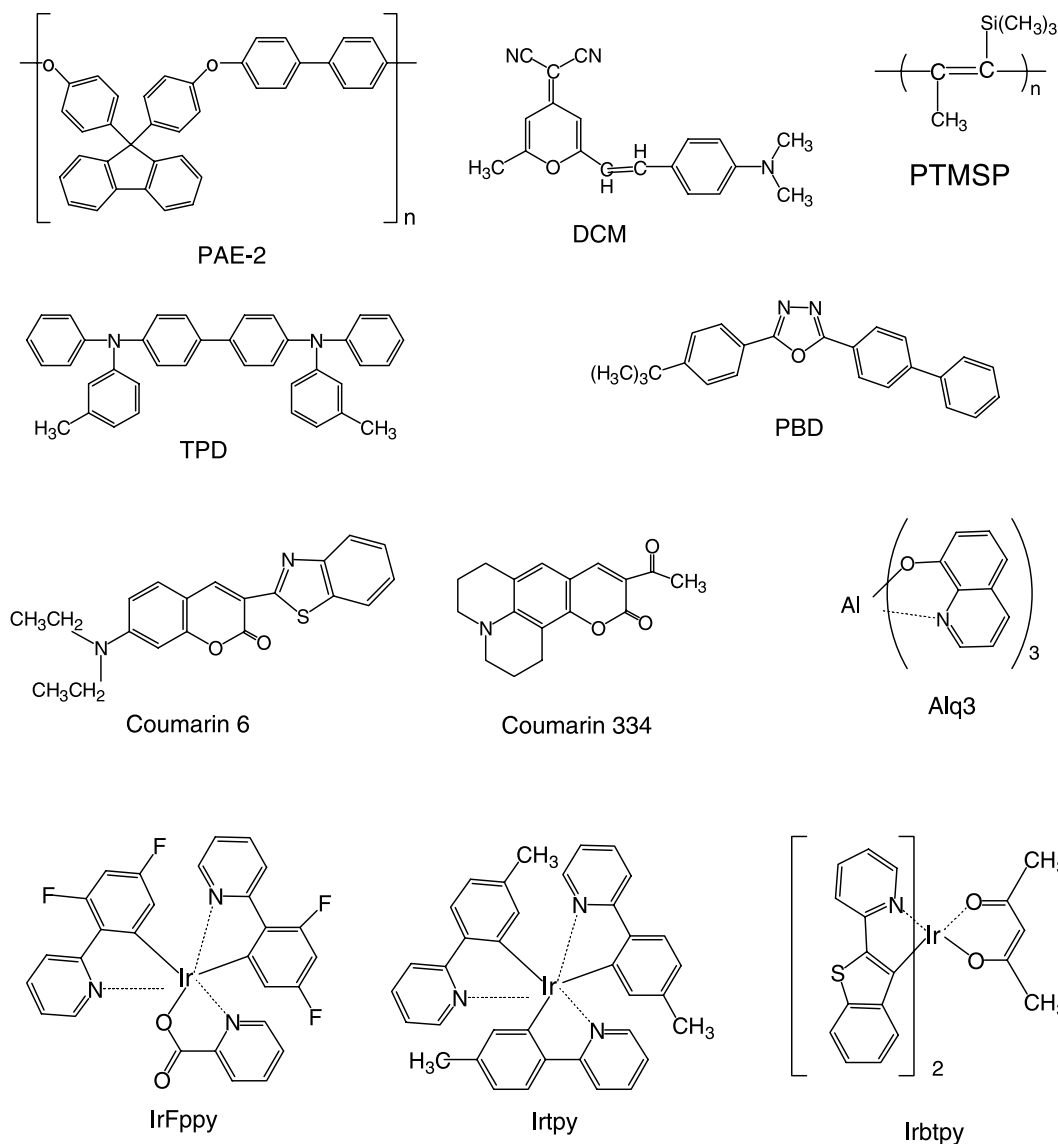


Fig. 2. Chemical structures of materials used for OLED evaluation.

case of Al cathode, a layer of 100 nm thick Al was evaporated in an evaporator without glove box inert atmosphere protection. In the case of Mg and Ca, the samples were transferred into the chamber of a vacuum evaporator that was located inside an argon atmosphere dry box. A layer of 20 nm thick Ca or Mg was vacuum deposited at about  $1 \times 10^{-7}$  Torr through the mask, and another layer of 100 nm thick silver (Ag) was deposited on top of the Ca or Mg layer to lower resistance and provide protection. Tests of the devices were carried out in air at room temperature. The thicknesses of the films were measured on a KLA Tencor P15 surface profilometer. Current–voltage characteristics were measured on a Keithley 2400 Source Meter. EL spectra were recorded with the InstaSpec IV CCD camera. The EL emission power was measured using a Newport 2835-C optical power meter with a calibrated photodiode. Brightness was calculated from the emission power and EL spectra of the devices, assuming Lambertian distribution of the EL emission [27].

### 3. Experimental results

The investigation of the properties/miscibility of PAE-2 and electroactive compounds was experimentally determined for PAE-2/Coumarin 6 blends dissolved in several solvents and then meniscus coated onto glass slides. The thin coatings were devolatilized, removed from the slide and tested in a differential scanning calorimeter for the glass transition temperature and crystallization behavior. The meniscus coated films removed from the glass slides exhibited brittle, but coherent properties vastly superior to unblended Coumarin 6, which of course, had no useful film properties. The  $T_g$  results shown in Fig. 3 demonstrate the miscibility of the samples as single  $T_g$  values were observed and show that the Coumarin 6 sample does significantly depress the PAE-2  $T_g$ . The crystallization kinetics shown in Fig. 4 demonstrate PAE-2 depresses the crystallization rate and degree of Coumarin 6 such that amorphous samples are obtained at  $> 60$  wt% PAE-2. It must

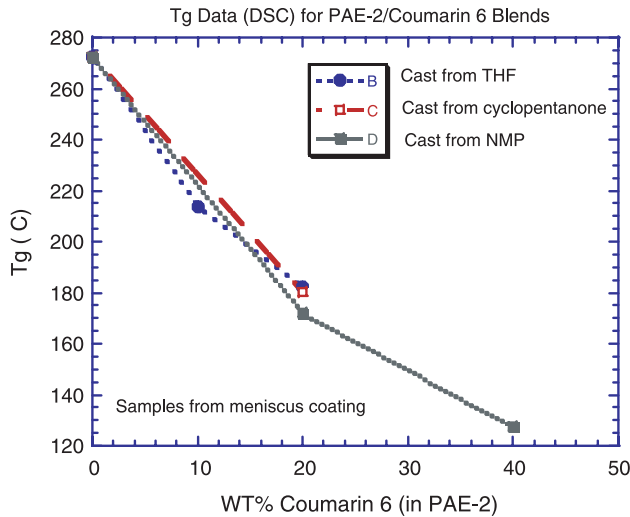


Fig. 3.  $T_g$  results (DSC) for PAE-2/Coumarin 6 blends.

be noted that the spin coating process offers a more rapid solvent removal than meniscus coating thus amorphous samples would be expected at lower PAE-2 contents for the films employed in LED devices in the experiments to be discussed.

The initial evaluation of this concept involved samples of PAE-2 with TPD levels of 5, 10, 15, and 20 wt% (based on solids content of PAE-2 and TPD) combined with 1.5 wt% Coumarin 6 (based on total solids). The LED devices were prepared by spin coating solution ( $\sim 2$  wt% solids) in chlorobenzene onto ITO coated glass substrates. Mg/Ag layers were applied via thermal vacuum deposition. Under forward bias (Ag connected to the negative electrode and ITO connected to the positive electrode), current–voltage measurements were obtained as shown in Fig. 5. The results show a percolation threshold in the range of 15 wt% TPD and thus in agreement with prior data using phenylene vinylene oligomers/DCM laser dye in a polystyrene matrix [9] and predictions of the deGennes percolation theory [10]. Above the onset voltage green light emission was observed. The next series of

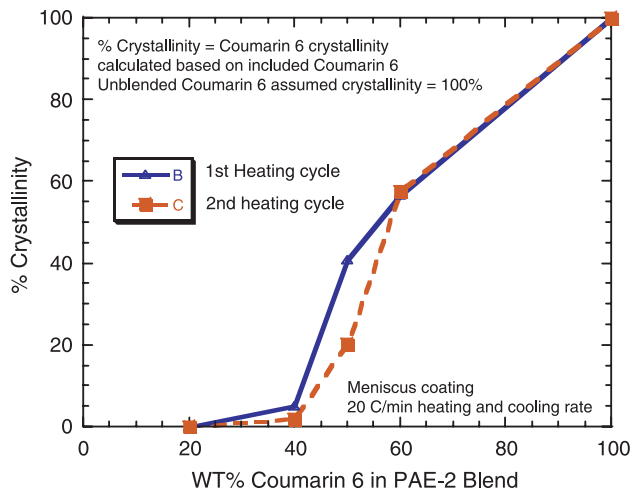


Fig. 4. Crystallinity results (DSC) on PAE-2/Coumarin 6 blends.

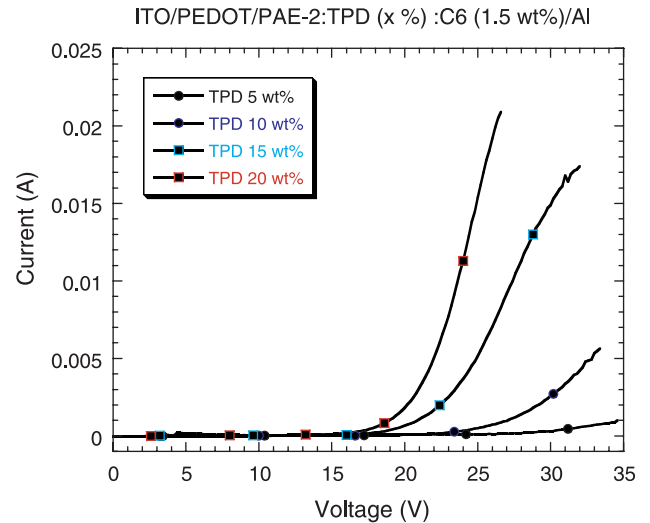


Fig. 5.  $IV$  curves of ITO/PEDOT/PAE-2:TPD:C6/Al devices at several loading level of TPD as shown in the legend.

experiments investigated the combination of electroactive materials in a common high  $T_g$  polymer matrix in a two layer LED device. PAE-2 was used to host a mixture of hole transporting TPD, electron transporting PBD and blue laser dye Coumarin 334 (C334). The weight ratio of PAE-2:TPD:PBD is 5:3:2. The doping ratio of C334 was 2.6 wt% based on the total solids. PEDOT was used as the HIL. Note that the high  $T_g$  polymer blends with the hole transporting and electron transporting species are listed throughout as wt ratios. When dopants are added the level is expressed in weight percent of total solids. A layer of 20 nm Ca was deposited as the cathode followed by a layer of 100 nm Ag as the cap. The finished device has a structure of ITO/PEDOT/PAE-2:TPD:PBD:C334/Ca/Ag. Fig. 6 shows the EL spectra and Fig. 7 the current density–voltage–brightness ( $J-V-B$ ) curve of the device. The EL spectra are dominated by the emission of the C334 dopant, with a peak wavelength at  $\sim 470$  nm. The turn-on voltage is 10 V, the maximum external quantum efficiency ( $\eta_{max}$ ) is 0.08%, and the maximum brightness is 640  $cd/m^2$ . The device

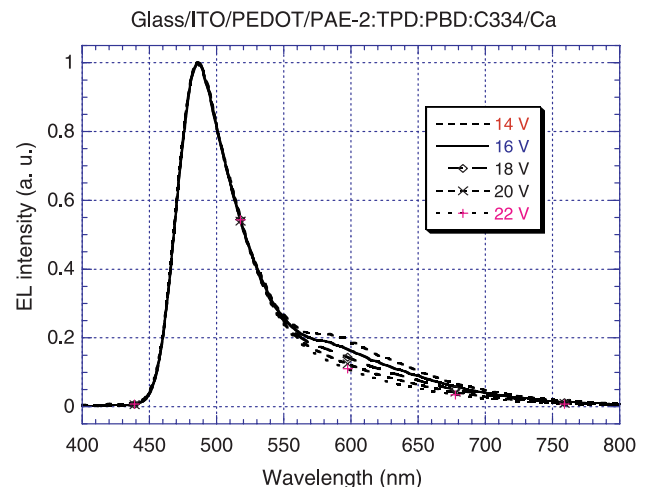


Fig. 6. EL spectrum (at different voltages) of a device with structure of ITO/PEDOT/P2:TPD:PBD:C334/Ca/Ag.

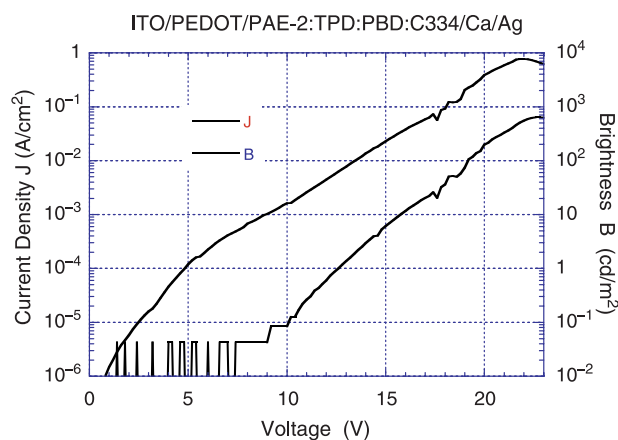


Fig. 7.  $J$ - $V$ - $B$  curve of a device with structure of ITO/PEDOT/PAE-2:TPD:PBD:C334/Ca/Ag.

performance is moderate due to the poor carrier transport ability of the PAE-2:TPD:PBD:C334 layer but well-demonstrates the basic concept of this paper.

$\text{Alq}_3$  is commonly employed as an electron transport/light emitting layer in OLED devices prepared using vacuum deposition procedures. Several papers note the desire to utilize  $\text{Alq}_3$  or other organometallic electroluminescent compounds in lower cost fabrication techniques such as spin coating and ink jet printing [28–30] and employ covalent bonded structures to polymer backbones. If sufficient solubility of  $\text{Alq}_3$  exists with a polymeric matrix there should be no need to provide covalent bonding and simple blending should accomplish the same objective. To demonstrate that  $\text{Alq}_3$  can be mixed with PAE-2 and spin coated for LED device application, 7.6 mg of PAE-2 and 7.7 mg  $\text{Alq}_3$  were dissolved in 1 mL of chloroform. LEDs with structure of ITO/PEDOT/PAE-2: $\text{Alq}_3$  (60 nm)/Ca/Ag were fabricated. Fig. 8 shows the EL spectrum of the devices. The devices turned on at 11–12 V, with  $\eta_{\text{max}}$  around 0.14%, and maximum brightness around 280  $\text{cd}/\text{m}^2$ . This demonstrates that  $\text{Alq}_3$  can be sequestered in a polymer matrix, without the need to chemically attach the  $\text{Alq}_3$  to the polymer backbone.

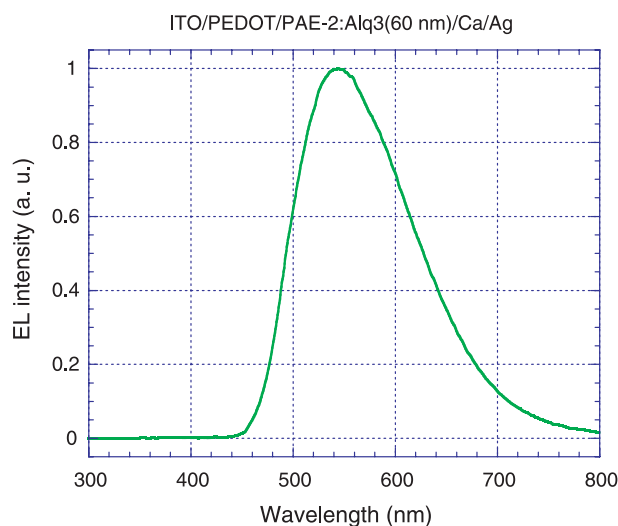


Fig. 8. EL spectrum of ITO/PEDOT/PAE-2: $\text{Alq}_3$ (60 nm)/Ca/Ag.

While the concept is demonstrated, further modifications in the LED construction would be desired to yield more favorable results.

PTMSP was also evaluated in this concept as it exhibits the highest free volume of known polymers [24] and thus has the capability to sequester large molecules, or higher loading level of electroactive molecules without a significant loss in properties. Both fluorescent and phosphorescent dyes were used as dopants. The fluorescent dye used was C6, and the phosphorescent dyes were blue, green and red emitting iridium complexes: iridium (III) bis(2-(4,6-difluorophenyl)pyridinato-N,C2) (IrFppy, ADS065BE from American Dye Source, Inc.), iridium (III) tris(2-(4-tolyl)pyridinato-N,C2) (Irtpy, ADS066GE from American Dye Source, Inc.), and iridium (III) bis(2-(2'-benzothienyl)pyridinato-N,C3')(acetylacetonate) (Irbtpy, ADS067RE from American Dye Source, Inc.), respectively. The phosphorescent dyes offer the advantage of being able to harvest both singlet and triplet excitons generated by the recombination of holes and electrons in an OLED device.

For device fabrication, 69.3 mg of PTMSP, 61.9 mg of TPD, and 64.3 mg of PBD were co-dissolved in 9.864 g of chlorobenzene as the host stock solution. The emitter dopants were then added to 2 g of the stock solution at a doping ratio (based on the total solids) of 0.73 wt% for C6, 6.4 wt% for IrFppy, 6.5 wt% for Irtpy, and 5.9 wt% for Irbtpy. Both single layer and double layer devices were tested. For the double layer devices, passive matrix grade PEDOT from Aldrich was used as the HIL. Table 1 summarizes the results. It is interesting to note that the single layer devices work relatively well compared to the double layer devices. The double layers with passive matrix grade PEDOT as the HIL show higher turn-on voltages, and higher efficiencies. It seems that the layer of PEDOT actually reduces the hole current injected into the light emitting layer. Due to the lower current, the maximum brightness values of the double layer devices are also lower. Fig. 9 shows the  $JVB$  curves of the Irtpy based single layer and double layer devices. The current of the single layer device under turn-on voltage was noisy. The introduction of a PEDOT layer in the double layer device resulted in a smooth current, but the current was also reduced.

The electroluminescence (EL) of PAE-2 with a high loading ratio of DCM was also studied. PAE-2, PBD and DCM with different weight ratios were dissolved in chlorobenzene and then spin coated onto PEDOT (Baytron<sup>®</sup> P (AS 4083)) coated ITO substrates as the emitting layer on a spin coater with the lid closed. The device structure is ITO/PEDOT/PAE-2:PBD:DCM/Ca/Ag. Fig. 10(a)–(d) shows the EL spectra of the devices (the weight ratios of the components are shown in the title of the graphs). All the spectra show two features: one peak at about 620 nm and another at about 780 nm. The PL spectra of the blend films are shown in Fig. 11. As can be seen, the PL spectra also show two features, although the relative strength of the two peaks is different from the EL spectra. From these data, it seems that DCM can form two types of phase structures in the film: amorphous phase emitting at 620 nm and another phase (heavily aggregated or even microcrystalline) structure emitting at 780 nm. As the voltage increases, the

Table 1

Performance of single and double layer devices using PTMSP as the high  $T_g$  polymer for sequestering small molecule electroactive charge transport materials and dopants

Device structure	V <sub>on</sub> (V) <sup>a</sup>	QE <sub>max</sub> (%) <sup>b</sup>	CE <sub>max</sub> (cd/A) <sup>c</sup>	B <sub>100</sub> (cd/m <sup>2</sup> ) <sup>d</sup>	B <sub>max</sub> (cd/m <sup>2</sup> ) <sup>e</sup>
ITO/C6 (0.73 wt%) in PTMSP:TPD:PBD (58 nm)/Ca/Ag	4.8	0.07	0.2	160	1870
ITO/Irtpy (6.5 wt%) in PTMSP:TPD:PBD (64 nm)/Ca/Ag	4.2	0.21	0.7	706	3840
ITO/Irtpy (5.9 wt%) in PTMSP:TPD:PBD (59 nm)/Ca/Ag	4.4	0.25	0.2	181	1330
ITO/IrFppy (6.4 wt%) in PTMSP:TPD:PBD (61 nm)/Ca/Ag	6.2	0.01	0.03	16	445
ITO/PEDOT (100 nm)/C6 (0.73 wt%) in PTMSP:TPD:PBD (58 nm)/Ca/Ag	5.9	0.09	0.2	171	258
ITO/PEDOT (100 nm)/Irtpy (6.5 wt%) in PTMSP:TPD:PBD (64 nm)/Ca/Ag	5.2	0.52	1.7	1570	2460
ITO/PEDOT (100 nm)/Irtpy (5.9 wt%) in PTMSP:TPD:PBD (59 nm)/Ca/Ag	5.7	0.61	0.44	314	568
ITO/PEDOT (100 nm)/IrFppy (6.4 wt%) in PTMSP:TPD:PBD (61 nm)/Ca/Ag	8.6	0.18	0.33	31.7	56.6

PTMSP:TPD:PBD = 35.4:31.7:32.9 (weight ratio).

<sup>a</sup> Turn-on voltage, the voltage required for the device to reach 1 cd/m<sup>2</sup>.

<sup>b</sup> Maximum quantum efficiency.

<sup>c</sup> Maximum current efficiency in cd/A—the ration of the brightness to the current density.

<sup>d</sup> Brightness at a current density of 100 mA/cm<sup>2</sup>.

<sup>e</sup> Maximum brightness.

relative strength of the 780 nm peak decreases. The peak at 780 nm is very interesting. Since the emission of this peak extends into NIR range, it might have some interesting application. This phenomenon has also some implication for PV device fabrication. Heavily aggregated or microcrystalline structure is desirable for PV application because of the higher mobility. The aggregation or microcrystalline structure could be due to the phase separation (crystallization) of DCM as the PAE-2 content in the films is much less than 50 wt%. Spin coating with the spin coater lid closed and with a high boiling point solvent such as chlorobenzene also helps the phase separation.

#### 4. Conclusions

The objective of this study was to demonstrate the concept of employing high  $T_g$  polymers as a matrix for sequestering large amounts of electroactive species for a light emitting layer of LED devices. While not optimized, the results demonstrate that spin coated layers can be obtained with high levels of electroactive species offering reasonable performance in LED devices. The same devices without the high  $T_g$  polymer offer no utility due to the crystallization and/or poor film properties when the same fabrication procedure is employed. The threshold concentration for light emission is in the range of 15 wt% of the electroactive species in the polymer matrix agreeing with earlier results on a lower  $T_g$  polymer (polystyrene) and also in agreement with the percolation threshold predictions of deGennes generally applied to heterogeneous systems. This approach allows for addition of hole transport, electron transport and dopant (e.g. laser dyes) species to a single layer and adjustment of the relative amounts

to optimize performance. One possibility that can be envisioned is white light emission using a multitude of electroactive species to yield a broad emission spectrum. The choice of the polymer matrix is important to assure that good miscibility is achieved with the electroactive species for LED performance. PAE-2 employed in these studies appears to meet that requirement while offering a high  $T_g$  (265 °C) such that large amounts of low molecular weight species do not yield blend  $T_g$ s lower than the desired use temperature. PTMSP, with a  $T_g > 330$  °C and a high free volume, also shows the ability

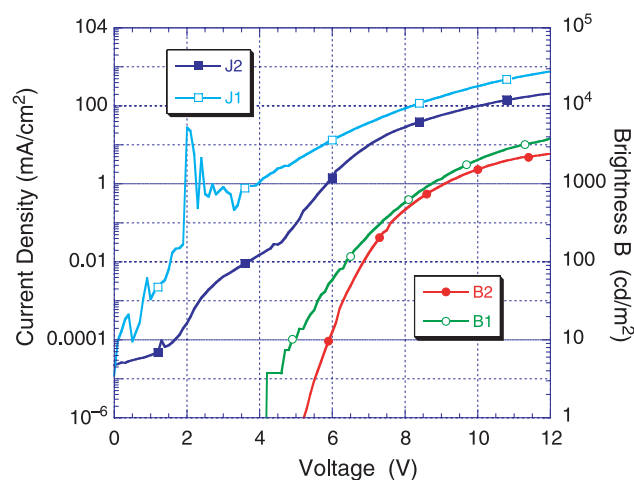


Fig. 9. Current density–voltage–brightness ( $JVB$ ) curves of a single layer and a double layer green emitting device. (a) ITO/Irtpy (6.5 wt%) in PTMSP:TPD:PBD (64 nm)/Ca/Ag and (b) ITO/PEDOT (100 nm)/Irtpy (6.5 wt%) in PTMSP:TPD:PBD (64 nm)/Ca/Ag (for interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

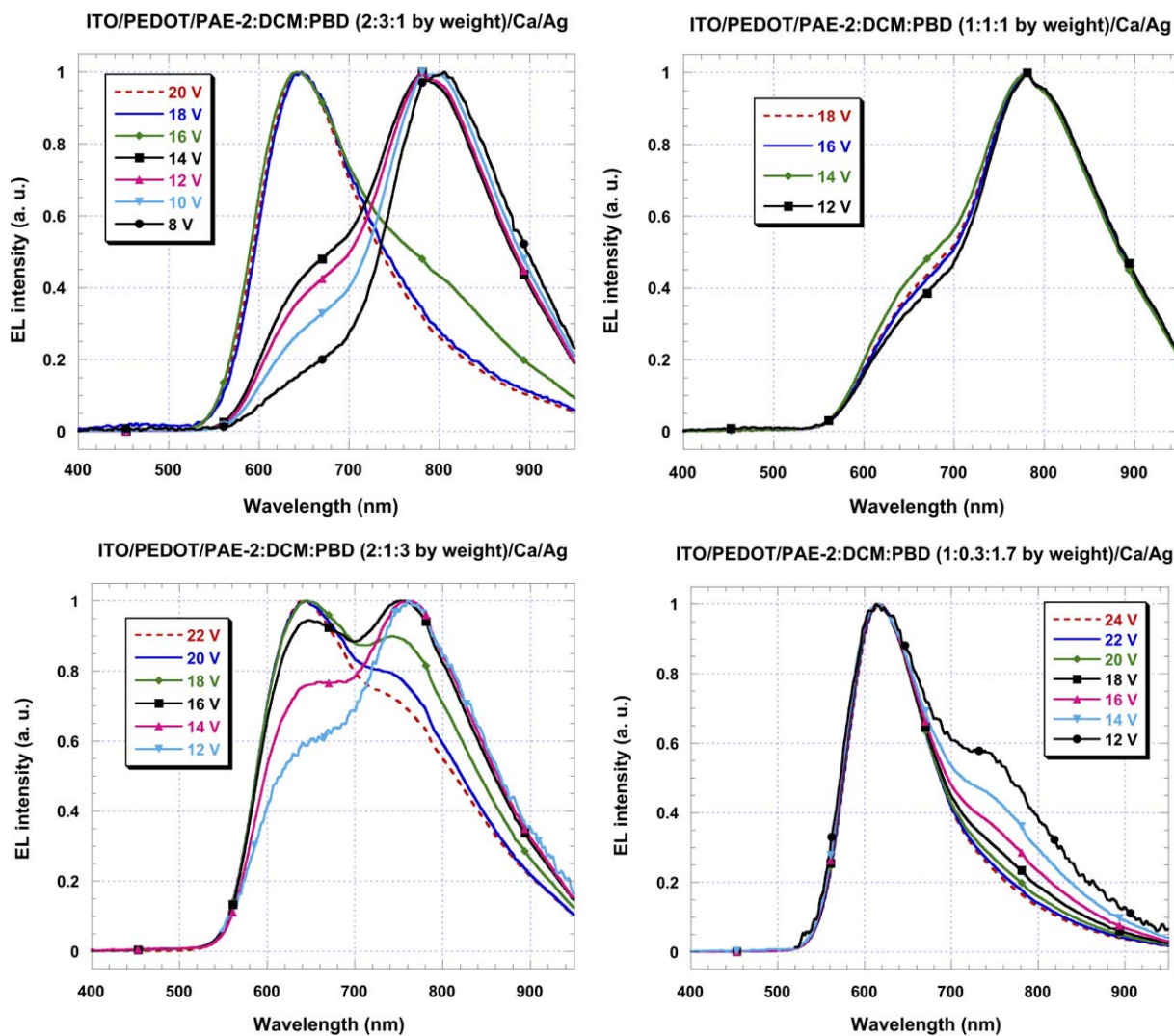


Fig. 10. (a–d) EL spectra of ITO/PEDOT/PAE-2:DCM:PBD/Ca/Ag at different voltages. The composition of the light emitting layers are shown in the title of the graphs.

to sequester large amounts of electroactive species and allow for good device performance. This method is analogous to approaches noted in the literature where the electroactive species are covalently bonded to a polymer backbone to yield the same objectives as this study. The blend approach, however, offers many advantages of which the ease to optimize the multitude of variables is paramount. This approach offers the advantage of easier and lower cost fabrication processes (spin coating, ink jet printing, roll-to-roll printing) over vacuum deposition processes commonly employed for low molecular weight electroactive species and achieves significant improvements in thin film mechanical properties. These advantages will be necessary for low cost flexible displays once other problems (such as flexible barrier film encapsulation) are resolved.

Optimization of the concept of this paper has not been conducted and further improvements would be expected both from the choice of the high  $T_g$  polymer and the electroactive species as well as the other layers of the device (e.g. hole injection layer). Device lifetime measurements were not made,

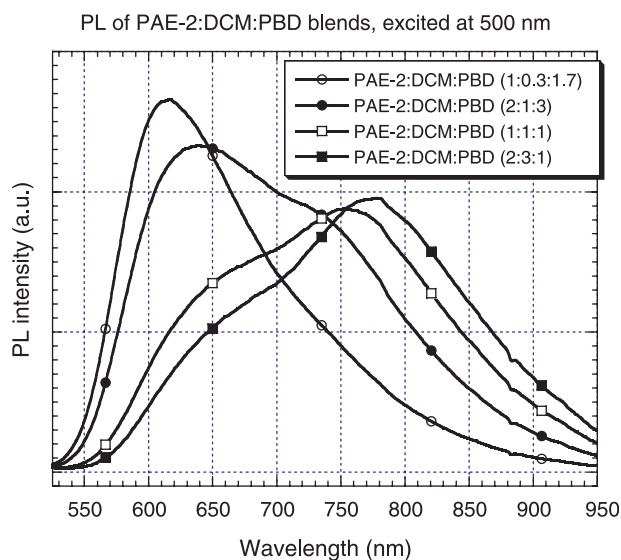


Fig. 11. PL Spectra of PAE-2:DCM:PBD blends.



and further optimization/characterization of this concept would require lifetime determination.

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