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Jeremiah K. Mwaura^a; Mathew K. Mathai^a; Changqing Chen^a; Fotios Papadimitrakopoulos^a

^a Nanomaterials Optoelectronics Laboratory, Department of Chemistry, Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut, USA

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Light Emitting Diodes Prepared from Terbium-Immobilized Polyurea Chelates

Jeremiah K. Mwaura, Mathew K. Mathai, Changqing Chen,
and Fotios Papadimitrakopoulos*

Nanomaterials Optoelectronics Laboratory, Department of Chemistry,
Polymer Program, Institute of Materials Science, University of Connecticut,
Storrs, Connecticut, USA

ABSTRACT

This article describes the synthesis and application of poly(1,4-phenylene-2,6-pyridylurea) (MCPU) as a charge transporting and rare earth metal chelating host matrix for organic light emitting diodes (OLEDs). The chelation between MCPU and Terbium (Tb^{3+}) (the rare earth metal used in this study), is facile in nature and persists in thin films obtained by spin coating onto various substrates. Multiple polymer chelating moieties at each Tb ion site may derive from MCPU repeat units from a single polymer chain or two polymer chains, and their respective structures are proposed. The emissive properties of these films in the presence and absence of Terbium (Tb^{3+}) were characterized by steady state UV-VIS absorption spectroscopy and photoluminescence (PL) spectroscopy. The PL emission from Tb(MCPU) films indicate contribution from both the host MCPU and the Tb ions. The incorporation of these films in OLEDs employing different device architectures yields electroluminescence spectra, which show the characteristic emission of the Tb ions but no emission from the host polymer matrix. Although these devices are not optimized, they exhibit an order of magnitude higher external quantum efficiency as compared to

*Correspondence: Fotios Papadimitrakopoulos, Nanomaterials Optoelectronics Laboratory, Department of Chemistry, Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, CT 06269-3136, USA; Fax: 860-486-4745; E-mail: papadim@mail.ims.uconn.edu.



that of conventional aluminum *tris* 8-hydroxyquinoline (Alq_3) based OLEDs, at low current densities.

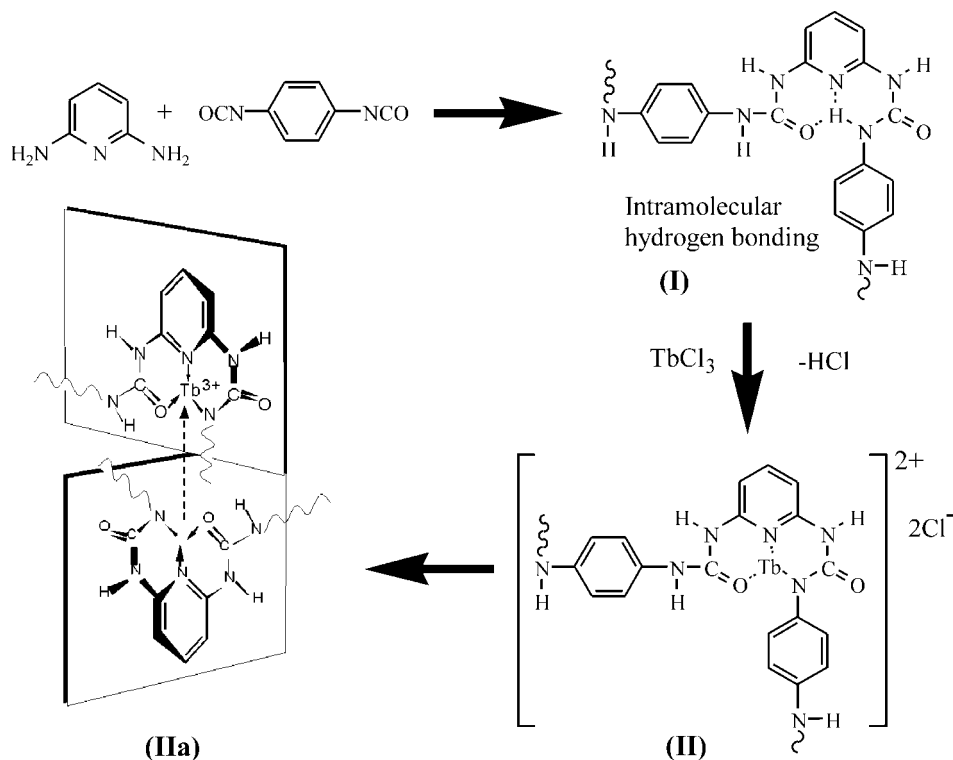
Key Words: Terbium; Chelation; Lanthanide; Rare earth metals; Electroluminescence; Organic light emitting diodes; Aromatic polyureas.

INTRODUCTION

Organic-lanthanide ion coordination complexes have attracted much attention in recent years due to their potential application as emitters in the development of electroluminescent devices.^[1–5] The luminescent properties of lanthanide metals have been used in applications including many efficient emitting systems such as solid-state lasers, optical communication amplifiers, cathodoluminescence display phosphors, as well as in biological applications as efficient labels in immunoassays.^[6–9] There are several advantages of using lanthanide metals due to their unique characteristics such as strong narrow-band ligand-sensitized cation based emission as well as long excited-state lifetimes.^[10–12] This ligand assisted emission employs several chelating agents for the sensitization of the well known lanthanides emitters, Tb (III) and Eu (III), such as β -diketones, bipyridines, pyridine carboxylic acids, as well as cryptands, calixarines, crown ethers and cyclodextrins.^[9,12–14] With ligands that do not satisfy all the La^{3+} ion's coordination numbers (believed to be eight or nine), water or aqua ions bind to the metal ion to fill up the coordination sphere.^[9,12–14] One way to protect the metal cation center from moisture (which reduces fluorescence intensity) is incorporating the chelates in inorganic matrices such as sol-gel silica.^[15,16] This has, however, been found to reduce luminescence intensity due to dilution, which has led to efforts in designing chelating ligands which simultaneously protect the metal ion from moisture while preserving the original photo-physical characteristics of the complex.^[15,16]

We have recently demonstrated that polyureas synthesized from 2,6-diaminopyridine are efficient metal-chelating agents.^[17] In particular, semi-rigid polyurethane-ureas based on 2,6-diaminopyridine, 1,6-diisocyanato hexane, and α,ω -hydroxyl terminated poly(ethylene glycol), can be assembled in a layer by layer format, in anhydrous solvents with a terbium salt to produce highly luminescent multilayer films. A strong green emission from these assemblies is characteristic of Tb^{3+} ion. This type of metal-chelation assemblies can be applied in the fabrication of organic light emitting diodes (OLEDs). Although the segmented polyurethane urea was proved appropriate for self-assembly of chelate films, it was unsuitable for OLED application due to its poor charge transport properties arising mostly from being non-conjugated. With this in mind, we synthesized a related metal-chelating aromatic urea, poly(1,4-phenylene-2,6-pyridylurea), as shown in Sch. 1, to improve charge transport efficiency in OLED devices and to utilize the subsequent Tb^{3+} /polyurea chelate as an emitting layer in the devices. In the most common design of lanthanide chelate based devices in the literature, the luminescent chelates are doped in appropriate hole charge transporting polymers or other small compounds mainly to minimize concentration quenching.^[2,3,18–21] In the chelate system described here, the polyurea takes on the roles of both macro-ligand and matrix for the luminescent lanthanide metal ions in OLEDs incorporating the same as the emissive layer.





Scheme 1. Synthesis of poly(1,4-phenylene-2,6-pyridylurea) **I** and subsequent chelation with Tb³⁺ **II** and **IIa**.

EXPERIMENTAL

Poly(1,4-phenylene-2,6-pyridylurea) (**I**) was synthesized through simple condensation polymerization of metal-chelating 2,6-aminopyridine and 1,4-phenylenediisocyanate. 2,6-diaminopyridine (10 mmoles) and 1,4-phenylenediisocyanate (10 mmoles) were each dissolved in 10 mL of distilled dimethyl formamide (DMF) and bubbled with N₂ for 30 min. Then, the 2,6-aminopyridine solution was cannulated into the diisocyanate solution and the mixture stirred for 2 h while maintaining N₂ bubbling. The resulting turbid suspension was poured into 400 mL of methanol and the white powder polymer was filtered, washed several times with methanol and vacuum dried overnight. The polymer molecular weight was found to be 18.7 Kdalton (with a polydispersity index of 1.15) as determined by size exclusion chromatography in DMF. The Tb-polyurea chelate [Tb(MCPU)] was prepared by adding different amounts of TbCl₃ to a solution of the polymer in DMF. For the device reported here, the molar concentration of terbium to polymer (based on the polyurea repeat unit) was optimized as 10%. Without isolating the resulting chelate, the solution was used to prepare films through spin casting.

This method of forming films based on Tb-polyurea chelates was then utilized to fabricate organic light emitting diodes. Indium tin oxide (ITO) patterned glass substrates



were purchased from Thin Film Devices. The Tb(MCPU) chelate was spin coated onto ITO (anode) substrates, which have been cleaned with solvents and oxygen plasma, to make a ~ 1500 Å thick film. Subsequent layers were thermally evaporated in an Edwards 306 thermal evaporator containing multiple sources at a pressure of 5×10^{-6} Torr. Two types of device configuration were fabricated. For the first set of devices, only the cathode consisting of a thin (10 Å) layer of CsF followed by 1000 Å of Al was evaporated on the Tb-polymer chelate films. The configuration for these devices was: (+) ITO/Tb(MCPU) (1500 Å)/CsF (10 Å)/Al (-) (1000 Å).

For the second set of devices, a 200 Å thick film of electron injecting and hole blocking 2,9-dimethyl-4,7-diphenyl-1,10 phenanthroline or bathocuproine (BCP) was first evaporated onto the Tb(MCPU) layer in order to better confine the recombination region and prevent light quenching from exciton migration to the cathode. This was then followed with the cathode consisting of a thin (10 Å) layer of CsF followed by 1000 Å of Al. Thus the device schematic is ITO/Tb(MCPU) (1500 Å)/BCP (200 Å)/CsF (10 Å)/Al (1000 Å).

For comparison of device performance, another set of devices based on Aluminum *tris*-(8 hydroxyquinoline) (Alq_3) were also fabricated. The device architecture in this case is ITO/NPB/ Alq_3 /CsF/Al where NPB (*N,N'*-Bis(naphthalen-1-yl)-*N,N'*-bis(phenyl)benzidine), is the hole transporting layer.

Following the sequential thermal evaporation of these layers the devices were transferred to a nitrogen glove box for characterization without exposing them to air. Device characterization is carried out with a Hewlett Packard 4155A semiconductor parameter analyzer and a Newport UV 818 photodetector. Electroluminescence spectra are collected by an MS 125 spectrograph coupled to a CCD IV array detector by Thermo Oriol. UV-VIS absorbance and photoluminescence spectra of the chelate films spin-cast on glass substrates were acquired through a Perkin-Elmer Lambda 6 Spectrometer and Perkin-Elmer LS-50 spectrophotometer, respectively. In order to further probe the energy potential for charge carriers within the Tb(MCPU) complex, cyclic voltammetry (CV) was carried out. Cyclic voltammetry was performed on a BAS 50 W system with a conventional three-electrode cell in a solution of 0.1 M Tetraethylammonium tetrafluoroborate (TEATFB) as the electrolyte in nitrogen-flushed, spectrophotometric grade DMF at a scan rate of 100 mV/s. The concentration of electroactive species was approximately 1 mg/mL.

RESULTS AND DISCUSSION

The synthesis of the metal chelating polyurea (MCPU) (I) and subsequent chelation with terbium salt is shown in Sch. 1. The metal complexation of (I) with Tb^{3+} occurs via removal of the acidic proton from the (I) isomer, based on Tb^{3+} ligand binding preference of oxygen over nitrogen. From molecular simulation (using Cerius² software) we believe that up to two macro-ligands can chelate with the metal cation in a manner presented in Sch. 1. UV-VIS spectra (normalized) of the polymer and Tb/polymer chelate spin-cast films on a glass substrate are shown in Fig. 1. The absorbance bands of the polymer macro-ligand are centered ~ 315 nm ($\pi-\pi^*$) and 280 nm ($n-\pi^*$). A small absorption peak at 360 nm on the Tb/polymer chelate is attributed to the complex formation. When excited at 315 nm the pristine polymer emits at 365 nm as can be seen in Fig. 2. Light emission in lanthanide chelates, involves intersystem crossing from the singlet excited state to the lowest triplet state on the ligand, followed by intramolecular energy transfer from the



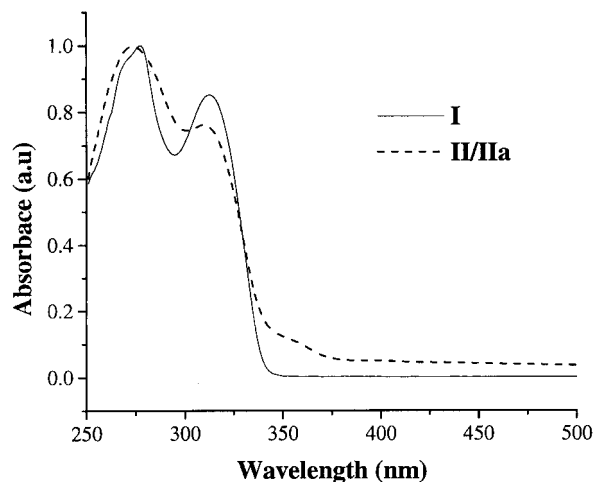


Figure 1. Normalized UV-VIS absorption spectra of poly(1,4-phenylene-2,6-pyridylurea) **I** (—) and the terbium/polyurea chelate **II** and **IIa** (---).

ligand to the highly localized $4f$ orbital levels of the rare-earth metal ion.^[11,22] The photoluminescence (PL) (excitation at 315 nm) of the chelate film (Fig. 2) shows the characteristic emission peaks (at 490, 545, 585, and 620 nm) from Tb^{3+} emanating from $^5D_4 \rightarrow ^7F_j$ ($j = 6, 5, 4,$ and 3) transitions, respectively. The broad emission peak centered at 430 nm is attributed to fluorescence from weakly chelated polymer in the presence of the heavy metal ion effect. This effect is not observed for layer-by-layer (LBL) assembled films^[17] which are believed to lead to complete chelation as opposed to the spin coated films used in this study. This is because in the LBL assembled case, weakly chelated ions

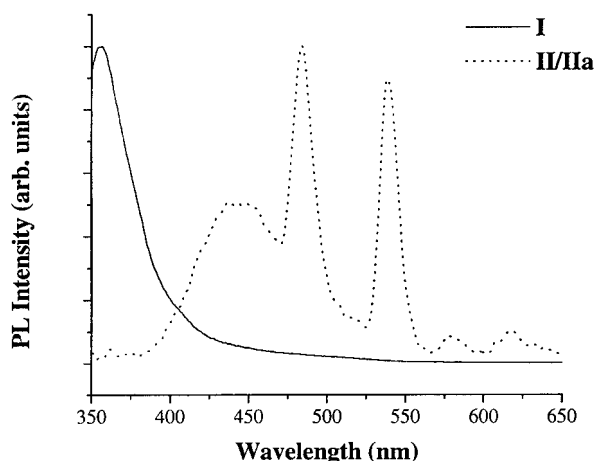


Figure 2. Normalized photoluminescence spectra ($\lambda_{exc} = 315$ nm) from films of poly(1,4-phenylene-2,6-pyridylurea) **I** (—) and the terbium-polyurea chelate **II** and **IIa** (---).



are readily removed in the washing steps between each cycle of layer deposition. This is not the case for spin coated films, where upon solvent (DMF) evaporation, not all Tb ions have assumed equilibrium positions in strong binding arrangements.

The Tb(MCPU) film spin coating technique was then applied to the fabrication of OLEDs without/with the utilization of a BCP layer as described in the experimental section. Figure 3 illustrates the configuration of the OLED device with BCP and the alignment of the energy levels as determined from CV and literature.^[23] As observed, there are large energy barriers for injection of the different charge carriers into the Tb(MCPU) layer. The barrier for hole injection at the ITO/Tb(MCPU) layer is 1 eV while that for the injection of electrons is 1.4 eV. The presence of BCP also enables the blocking of holes at the Tb(MCPU)/BCP interface by a HOMO offset of 1.1 eV.

Figure 4 shows the current density–voltage (I – V) and luminescence–voltage (L – V) for the devices, ITO/Tb(MCPU)/CsF/Al and ITO/Tb(MCPU)/BCP/CsF/Al. In the case of the first device, a gradual turn on in the current is observed at a voltage of c.a. 7 V. However, this device did not emit light. The reason for this can be the formation of a recombination interface for holes and electrons, which is closer to the cathode. Besides this, the longer lifetime of the triplets suggests a greater extent of migration to the metal electrode and subsequent quenching. In order to overcome this an additional BCP layer is inserted

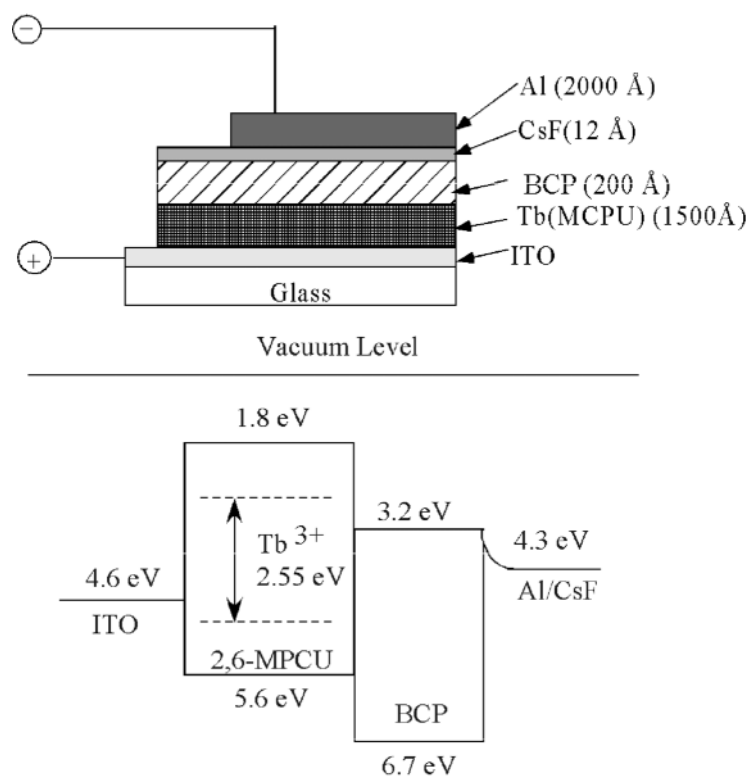


Figure 3. Configuration of a typical OLED fabricated incorporating the Tb(MCPU) chelate film and the band diagram for the same.



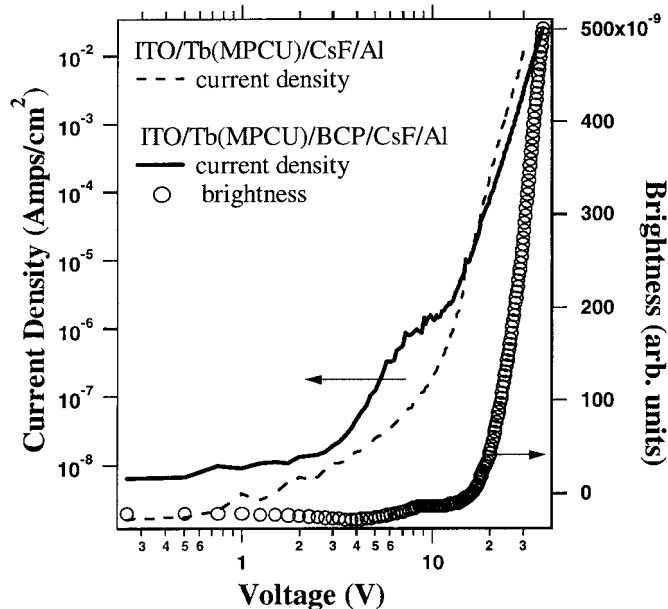


Figure 4. Current density–voltage and brightness–voltage characteristics for the ITO/Tb(MPCU)/BCP/CsF/Al device and current density for the non-light emitting ITO/Tb(MPCU)/CsF/Al device.

between the cathode and the Tb(MCPU) layer. The presence of the BCP layer in this second device facilitates electron injection at lower applied electric field.^[23] At an applied voltage >3 V, the hole and electron injection are induced in the device as can be seen by the increase in current above this voltage in the I - V curves. At this point (3 V), light emission resulting from the relaxation of exciton created when the holes and electrons recombine in the terbium chelate layer begins, as characterized by the luminescence–voltage (L - V) curve. The L - V curve indicates the initial light turn-on for this device at 3 V with electroluminescence (EL) intensification at the shoulder observed ~ 13 V. This intensification corresponds to the apparent imbalanced charge injection, demonstrated by a shoulder in the I - V curve at 13 V. The presence of this shoulder is not presently understood but could originate due to temporal space charge effects, which are overcome at higher applied fields.

The EL spectrum of the light emitting device as shown in Fig. 5 exhibits the distinct emission peaks characteristic of Tb^{3+} ion, with the 545 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition) peak dominating.^[5] In contrast to the PL (Fig. 2) exhibited by films of this Tb-chelate where emission from weakly chelated macro-ligands is observed, no EL component from the polyurea ligand is evident from the spectrum. Evidently, the macro-ligands in this complex, chelated and/or unchelated only transport charge but the hole/electron recombination (exciton) occurs in the metal cation emitting levels and hence the emission only from the cation (characteristic of lanthanide chelates) is observed. The peak at 490 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_6$ transition) appears to be less in intensity on the EL spectrum as compared to PL. This has been observed with other terbium chelates and although it is not yet well understood, it has been attributed to the possibility of some change in coordination of the terbium ion during device preparation.^[1]



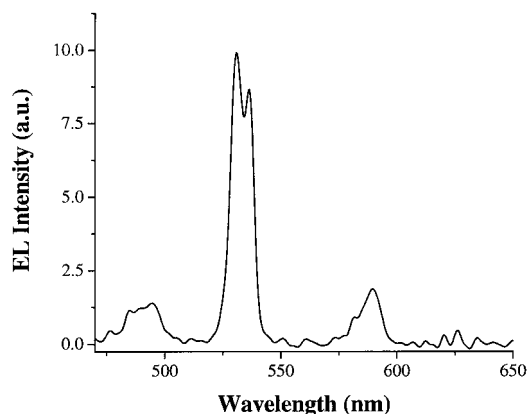


Figure 5. Electroluminescence (EL) spectrum from the device, ITO/Tb(MCPU)/BCP/CsF/Al.

The device quantum efficiency [in arbitrary units (a.u.)] vs. current density is shown in Fig. 6 and is compared to that of a typical Alq₃/NPB device which exhibits an external quantum efficiency in the range of 0.5 to 1%.^[24] This efficiency is calculated by dividing the photodiode current by the device current. After reaching a maximum value, the efficiency decreases as current density increases. At its maximum, an external quantum efficiency of ~0.07 a.u. at 0.5 mA/cm² was obtained, which falls off to ~0.0002 a.u. at 20 mA/cm². The decrease in efficiency can be attributed to the increased charge carriers quenching due to the Tb chelate excited states as current density increases, and/or due to quenching of emission at the ITO electrode. Due to long luminescence lifetimes of lanthanide complexes, the probability of quenching by charge carriers is increased, a

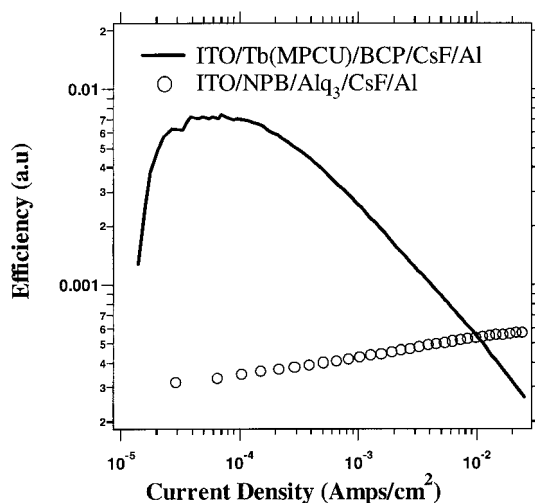


Figure 6. Comparison of quantum efficiencies between the terbium chelate device (ITO/{2,6-MCPU}Tb/BCP/CsF/Al) and Alq₃ device (ITO/NPB/Alq₃/CsF/Al).



phenomenon that has been observed in other lanthanide chelate's devices.^[1,4] Compared to a typical aluminum quinoline (Alq_3) device, which is seen to have a slowly increasing efficiency till ca. 0.0005 a.u. at 20 mA/cm^2 , the terbium chelate device described here demonstrates over an order of magnitude higher quantum efficiency at same current densities, as shown in Fig. 6. This however, does not constitute overall better device efficiency for the terbium device, since to obtain the same current density through the device, the Alq_3 device runs at much lower applied voltage ($\sim 3 \text{ V}$) while for the terbium device the applied field was 20 V at maximum quantum efficiency. The comparatively poorer charge transport properties of the polyurea constituting the terbium chelate devices, account for the high fields required to operate the devices.

CONCLUSION

In conclusion, a novel polymeric Tb(III) complex was synthesized and utilized to make EL devices. Utilizing a polymeric ligand with the dual role of sensitizing metal-cation based emission and as a charge transport layer offers promise for simplifying fabrication of green emitting OLEDs. Although working devices were successfully fabricated with over an order of magnitude improvement in external quantum efficiency with respect to that of Alq_3 based OLEDs, these devices required high driving fields due to the poor charge transport properties of the polyurea macro-ligand.

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