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Synthesis, morphology and optoelectronic properties of tris[(*N*-ethylcarbazolyl)(3′,5′-hexyloxybenzoyl)methane](phenanthroline)-europium†

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The complex tris[1(*N*- ethylcarbazolyl)(3′,5′-hexyloxybenzoyl)methane](phenanthroline)europium 1 incorporates a phenanthroline ligand for electron transport and a carbazole fragment in the diketonate ligand for hole transport; furthermore, the six hexyloxy groups prevent crystallization and allow for the formation of transparent clear films directly from solution; the photoluminescence from films of 1 is nearly monochromatic, characteristic of the europium ion and proceeds with an efficiency of 50(3)%; light emitting diodes(LEDs) were fabricated using the simplest possible device architecture comprising an anode (ITO), a layer of 1 and a cathode (Ca); a second LED configuration with a PVK layer on top of the ITO was also investigated; the performance of the two types of devices is discussed.

Europium tris(β-diketonate) complexes are finding innovative applications as the electroluminescent layer in molecular light emitting diodes (LEDs).[1] Since the emission from these complexes stems from transitions between f levels that are well protected from environmental perturbations by the filled $5s^2$ and $5d^{10}$ orbitals, the resulting emission bands (585 nm, ${}^5D_0 \rightarrow {}^7F_1$ and 617 nm ${}^5D_0 \rightarrow {}^7F_2$) are nearly monochromatic.[2] Color purity of this type is required for full color displays. Pure red, green and blue light can be obtained by the use of filters, albeit with a decrease in light output.[3]

Typically, LEDs using lanthanide-based materials are fabricated by vacuum deposition of the complex onto a suitable charge injection layer. To optimize charge balance, the best devices take advantage of a multilayer architecture.[4] We recently reported polymeric light-emitting diodes that emit pure red light with a 3.5 nm linewidth by making use of energy transfer from poly[2-(6′-cyano-6″-methylheptyloxy)-1,4-pheneylene] (CN-PPP) to europium complexes with β-diketonate and phenanthroline ligands.[5] In this approach, a film containing the polymer and the complex can be cast directly from solution thereby facilitating fabrication. Efficient excitation transfer from CN-PPP results in complete quenching of the broad emission of the polymer and pure red Eu-based emission.

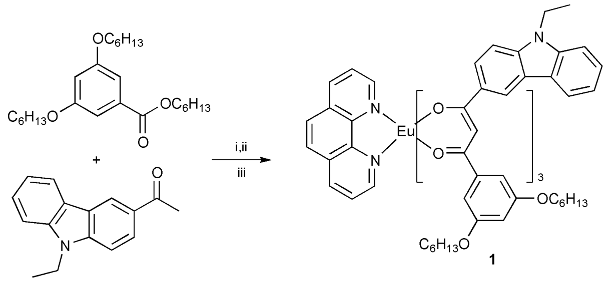
It occurred to us that it should be possible to design a ligand for europium that contained structural features for optimizing charge transport across the bulk and that gave the complex topological attributes which would discourage crystallization. The latter requirement was incorporated so as to obtain stable glasses and uniform optical quality thin films directly from solution. As our target, we chose the complex tris[(*N*-ethylcarbazolyl)(3′,5′-hexyloxybenzoyl)methane](phenanthroline)europium **1** (Scheme 1). The phenanthroline ligand was included since it is thought to enhance the electron transport of the material.[6] A carbazole fragment was appended to the diketonate ligand with the intention of improving hole transport.[7] Finally the hexyloxy groups were introduced to prevent crystallization and to increase solubility in common organic solvents.

As shown in Scheme 1, the diketonate ligand is prepared by Claisen condensation of 3-acetyl-9-ethylcarbazole[8] and hexyl-3,5-hexyloxybenzoate in the presence of NaH. After refluxing in dimethoxyethane for 24 h, followed by acetic work-up and purification by chromatography, (*N*-ethylcarbazolyl)(3,5-hexyloxybenzoyl)methane is obtained in 24% yield. The europium complex **1** is prepared by taking advantage of well established protocols.[9] Deprotonation of three equivalents of (*N*-ethylcarbazolyl)(3,5-hexyloxybenzoyl)methane with an excess of NaOH, followed by treatment with $EuCl_3(H_2O)_6$ and finally phenanthroline affords **1** in 50% yield. Purification can be accomplished by precipitation from concentrated acetone solutions.

Compound **1** is a pale yellow powder, which by differential scanning calorimetry (DSC) shows a glass transition temperature at 65 °C. Powder diffraction experiments show no evidence of crystalline regions. The morphological properties of compound **1** make it possible to spin-cast clear transparent films directly from solution.

Fig. 1 shows the absorption and photoluminescence spectra of a thin film of **1**. The absorption onset at *ca.* 458 nm corresponds to a HOMO–LUMO energy difference of 2.71 eV. This value is also observed in the spectrum of the sodium salt of the diketonate ligand. Light absorption is therefore controlled by the ligand framework. The sharp emission at 612 nm is characteristic of the europium ion within a tris(β-diketonate)-phenanthroline environment. Therefore, the triplet level of the ligand is sufficiently high to allow energy transfer to the ion.[10] Use of an integrating sphere revealed that the solid state photoluminescence efficiency from films of **1** is 50(3)%. These measurements were made using the 351 nm line from an argon laser (intensity of 2.5 mW cm^{-2}), an integrating sphere, a high pass filter that blocks the laser line, and a silicon diode.[11]

The resistance to crystallization and exceptionally low self quenching of **1** prompted us to examine its electroluminescent properties. Two types of LED structures were fabricated.[12] In



Scheme 1 *Reagents and conditions*: i, NaH/dimethoxyethane; ii, NaOH, $EuCl_3(H_2O)_6$, ethanol; iii, phenanthroline, toluene.

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† Complete details for the synthesis of **1** (PDF). The material is available free of charge *via* the Internet at http://pubs.acs.org.

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the first device, a film of **1** (600 Å) was spin-cast directly onto the indium tin oxide (ITO) anode. The spin-casting solution was 1 wt% in toluene and was filtered through a 5 micron Nylon filter. The layer of **1** was subsequently dried under vacuum at ambient temperature for *ca.* 1 h. The calcium cathode layer was deposited as described previously and subsequently overcoated with aluminium.[12] This device has only a single layer and only one molecular component between the electrodes; *i.e.* the simplest architecture possible.

Fig. 2 shows the current–voltage curve of the single-layer device. Light emitted from this device is identical to the PL spectrum shown in Fig. 1. The turn-on voltage for current and luminance, is observed at *ca.* 5.3 V (8.8 mV $Å^{-1}$) and is similar in magnitude to many polymer LEDs and lower than many multilayer organic LEDs (OLEDs) prepared by sublimation. These characteristics demonstrate that the ligand design was successful in facilitating electron and hole injection and transport into and across the europium layer. At 15 mA cm^{-2}, the light output is 9 cd m^{-2} with an external EL quantum efficiency of 0.08%.

A second device architecture was fabricated in an effort to improve the device efficiency, and to gain insight into the mechanism of europium electroluminescence. In this archetecture, a layer of polyvinylcarbazole (PVK) (30 nm) was first spin-cast from a 2% solution of PVK in 1,1,2,2-tetrachloroethane on top of the ITO-glass substrate and, after drying at 60 °C for 1 h, a 700 Å layer of **1** was spin-cast as before. The cathode layer is the same as in type 1. Only emission from Eu was observed, *i.e.* identical to Fig. 1. Fig. 3 shows the current–voltage relationship for this device. Compared to the single layer device, the turn-on voltage is higher, *ca.* 8.7V (8.75 mV $Å^{-1}$), owing to the extra thickness introduced by the PVK layer; but both devices operate at equivalent field strengths. The device efficiency was improved considerably (50 cd m^{-2} at 15 mA cm^{-2})[13] with an external quantum efficiency of 0.3%. It is thought that the PVK layer acts both as a hole injection and an electron blocking layer[14] facilitating more balanced carrier injection from the anode and cathode.

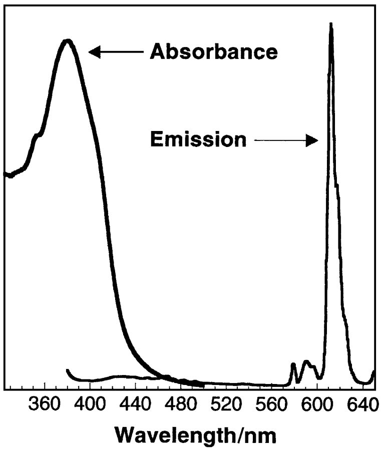

Fig. 1 Absorption and emission spectra of a thin film of **1**.

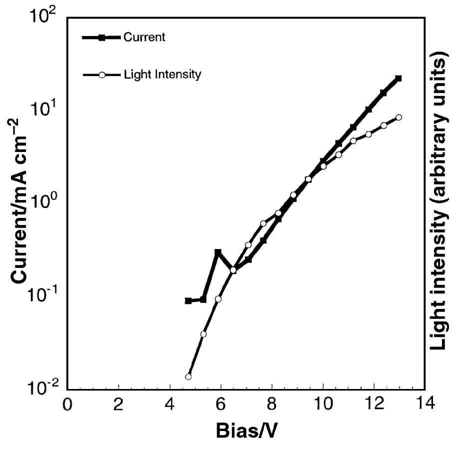

Fig. 2 Current–voltage curve of the device with configuration ITO/**1**/Ca.

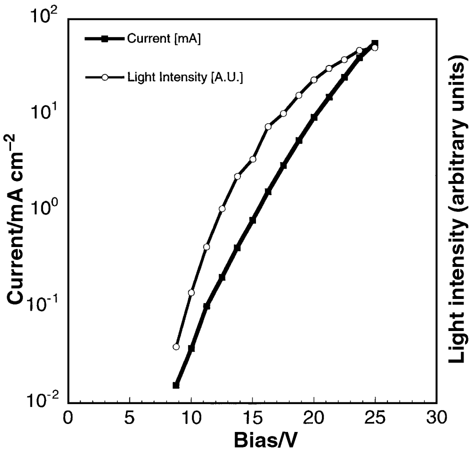

Fig. 3 Current–voltage curve of the device with configuration ITO/PVK/**1**/Ca.

In summary, it is possible to introduce structural attributes to the ligand framework of an europium complex that allow its use as the electroluminescent layer in a single component LED. The key design components include the use of hole and electron transport fragments, together with aliphatic sidegroups that lead to a stable amorphous phase. The film forming properties of **1** play an important role in device fabrication.

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13 Under these conditions the efficiency may be expressed as 0.33 cd A^{-1}. For comparison, trilayer devices containing a mixture of tris(1,3-diphenylpropane-1,3-dionato)(monophenanthroline)europium with PBD have been reported to exhibit efficiencies of 1.7 cd A^{-1} at 2.2 mA cm^{-2} and 0.16 cd A^{-1} at 290 mA cm^{-2}. See ref. 1(*b*).

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