

Modulated Infrared Electroluminescence From Organic Light-Emitting Diodes

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Abstract—Modulated infrared electroluminescence from organic light-emitting diodes (OLEDs) based on rare earth complexes (tris-dibenzoylmethanato-mono-bathophenanthroline) erbium or neodymium were fabricated. The modulations were realized by varying the device configuration and by varying an applied forward bias at room temperature. We found that the intensity of EL peak at 1.54 μm was reduced by a factor of almost 20 times as the Nd complex layer thickness in the OLEDs was increased from 1 nm to 5 nm. The intensity ratio of the 1.54 μm (Nd) to 1.06 μm (Er) decreases from 0.82 to 0.53 as the forward bias increases from 6.5 V to 18 V. The effects of the modulation of these IR emissions were also discussed.

Index Terms—Modulated infrared electroluminescence, organic light emitting devices, rare-earth complexes and recombination zone.

I. INTRODUCTION

NEAR INFRARED (NIR) emissive devices based on organic materials have been gaining widespread attention due to their low-cost and inherent physical flexibility. These devices have potential applications in the areas of optical communication, biological sensing and electrically-excited light emission. The most promising candidates for NIR emissive materials include rare-earth (RE) complexes, semiconductor nanocrystals with organic agents, organic infrared dyes [1]–[3] and recently, efficient organic phosphorescence materials [4], [5]. Amongst them, RE complexes display unique narrow band emissions that originates from the 4f transitions of the RE ions, these emissive bands span a wide wavelength range (from ultraviolet to NIR), which can be useful for many optoelectrical applications. NIR emissions from OLEDs based on Er, Nd, and Pr-complexes

have been reported [1], [6]–[8]. The RE-complex electroluminescence (EL) process proceeds with the excitation of both the singlet (S) and the triplet states (T) of the ligands; followed by an resonant energy transfer from the T_1 states to the RE ions. Hence, an internal quantum efficiency of 100% is achievable theoretically.

In the recent years, increasing demands for large transfer of information necessitates the use of multichannel wavelength division multiplexing (WDM) networks in the NIR range. To compensate for the intrinsic optical losses in these WDM circuits, optical amplifiers or light sources have to be incorporated in these multichannel circuits. However, it is neither convenient nor cost-effective to incorporate multiple light sources or amplifiers in these WDM circuits. Multiwavelength modulated organic light emitting diodes can offer an attractive solution to compensating the losses in these different channels by simply tuning the applied voltage. These methods will permit greater flexibility in achieving both channel selectivity and controlling the output intensity of individual channels in WDM circuits.

Color-tunable OLEDs have been realized in the visible range, most of them are based on altering the relative intensities of the multiband emissions. The tuning can be achieved by means of: modulating the bias polarity; controlling the energy offset in the small molecule or polymer OLEDs; or using stacked device architecture at room temperature [9]–[11]. In a previous work, we have reported on the broadening of the infrared emission bands of OLEDs based on mixing Er and Tm complexes as the active medium. This suggests the possibility of realizing simultaneous multiple IR emissions over a broad spectral band via electrical excitation [12]. To date, there have been few reported work on the modulation of NIR emissions from OLEDs.

In this paper, we report on the results of modulated IR emission OLEDs made with (tris-dibenzoylmethanato-mono-bathophenanthroline) erbium ($\text{Er}(\text{DBM})_3\text{bath}$) and (tris-dibenzoylmethanato-mono-bathophenanthroline) neodymium ($\text{Nd}(\text{DBM})_3\text{bath}$). The IR emissions in $\text{Er}(\text{DBM})_3\text{bath}$ and $\text{Nd}(\text{DBM})_3\text{bath}$ based OLEDs can be achieved by adjusting the forward bias or varying the configuration of $\text{Er}(\text{DBM})_3\text{bath}/\text{Nd}(\text{DBM})_3\text{bath}$ layer thickness used in the devices. Both $\text{Er}(\text{DBM})_3\text{bath}$ and $\text{Nd}(\text{DBM})_3\text{bath}$ exhibit strong IR emissions (i.e., 1.064 μm and 1.3 μm for Nd^{3+} ion; 1.54 μm for Er^{3+} ion). The emission intensity of the Nd^{3+} at 1.064 μm is comparable to that of Er^{3+} at 1.54 μm under the same excitation condition, matching the spectral windows that are suitable for telecommunication applications.

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II. EXPERIMENTAL

The molecular structures of $\text{Er}(\text{DBM})_3\text{bath}$ and $\text{Nd}(\text{DBM})_3\text{bath}$ and the schematic energy diagram of the OLEDs are given in Fig. 1. These RE complexes were synthesized using a conventional method [13] and were employed as both the emitting and electron-transporting (ET) materials. In the case for the hole-transporting (HT) material, N,N' -Bis(3-methylphenyl)- N,N' -bis(phenyl)-benzidine (TPD) was used. Organic films and Mg:Ag (10:1) alloy cathode were deposited onto an indium-tin oxide (ITO) glass substrate $100/\square$ successively by thermal evaporation in a vacuum chamber at 2×10^{-4} Pa without breaking vacuum. A precise control the film thickness over the device configuration can be achieved. The evaporating rate was varied from 0.5 to 3 $\text{\AA}/\text{s}$ for the organic layers and 10 $\text{\AA}/\text{s}$ for the alloy cathode. The fabricated devices were encapsulated under a dry N_2 ambient in a glove-box to minimize the device degradation during the EL measurements. The device active area was 0.12 cm^2 .

An array detector (i.e., liquid N_2 cooled Ge detector and CCD detector) on a NIR 700–1600 nm Biorad PL-9000FT spectrometer was used for the measurements. The EL spectra obtained were the averaged over 20 measurements. There was no observable degradation of the devices when operating at 12 V and 18 V. Cyclic voltammeter measurements at room temperature were also performed to identify the energy gap and the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of $\text{RE}(\text{DBM})_3\text{bath}$. These were measured using an EG&G Model 283 potentiostat/galvanostat in a typical three-electrode cell with a working electrode (Pt wire), a reference electrode (Ag/AgCl, externally referenced against Fc/Fc⁺, 0.44 V), and a counter electrode (Pt gauze) under a nitrogen atmosphere at a sweeping rate of 100 mV/s. A solution of tetrabutylammonium perchlorate (TBAP) in anhydrous CH_2Cl_2 was used as the electrolyte. The LUMO and HOMO of $\text{RE}(\text{DBM})_3\text{bath}$ were found to be 2.8 eV and 5.9 eV, respectively. The devices were fabricated with a three layer structure: ITO/TPD(60 nm)/ $\text{Nd}(\text{DBM})_3\text{bath}(x \text{ nm})/\text{Er}(\text{DBM})_3\text{bath}(60 - x \text{ nm})/\text{Mg}:\text{Ag}(10:1, 150 \text{ nm})(x = 1, 5, 15, 20 \text{ nm})$.

III. RESULTS AND DISCUSSION

Fig. 2 shows the infrared EL performances as a function of the thickness of the middle-layer ($\text{Nd}(\text{DBM})_3\text{bath}$). All the spectra were normalized with respect to the 1.064 μm emission peak with the exception of the $x = 1 \text{ nm}$ case, where the intensity was divided by a factor of 10. The 1.064 μm emission originates from the ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{13/2}$ transition of the Nd^{3+} ions, while the 1.54 μm originates from the ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ transition of the Er^{3+} ions. All the spectra were measured under an applied voltage of 12 V with similar current intensities. When the $\text{Nd}(\text{DBM})_3\text{bath}$ thickness is ultra-thin (i.e., 1 nm), the 1.54 μm emission dominates (note that the intensity is divided by 10 times) while the 1.064 μm emission has almost vanished. The 1.064 μm emission intensity increases when the thickness of the $\text{Nd}(\text{DBM})_3\text{bath}$ layer was increased to 5 nm; while the

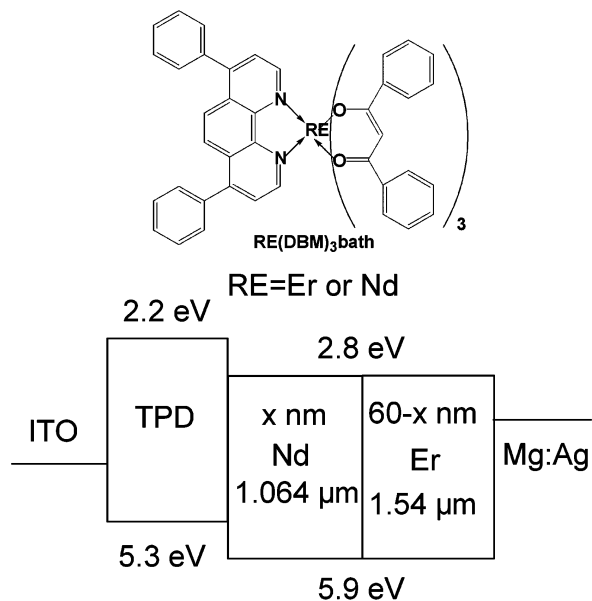


Fig. 1. The chemical structure of $\text{Er}(\text{DBM})_3\text{bath}$ and $\text{Nd}(\text{DBM})_3\text{bath}$, and the energy diagram of the OLEDs.

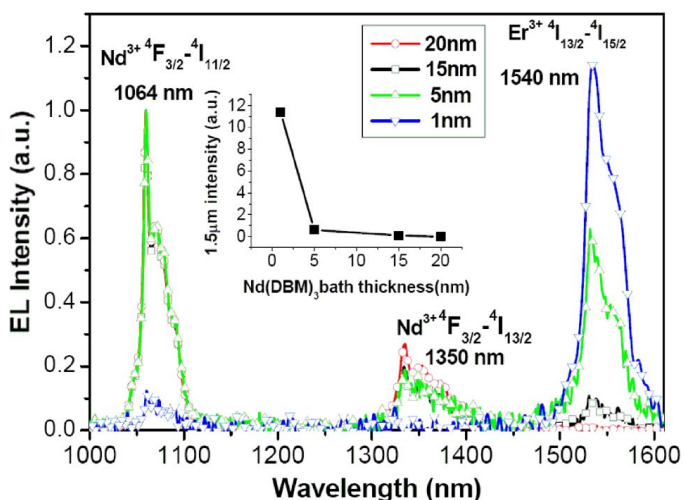


Fig. 2. The infrared EL emissions of OLED with structure: ITO(60 nm)/TPD(60 nm)/ $\text{Nd}(\text{DBM})_3\text{bath}(x \text{ nm})/\text{Er}(\text{DBM})_3\text{bath}(60 - x \text{ nm})/\text{Mg}:\text{Ag}(10:1, 150 \text{ nm})(x = 1, 5, 15, 20 \text{ nm})$, all measured at 12 V. In the case of 1 nm, the intensity was divided by a factor of 10. The insert Fig is 1.5 μm emission decrease with the middle layer $\text{Nd}(\text{DBM})_3\text{bath}$ thickness increasing.

1.54 μm emission becomes much weaker. When the thickness of this layer is increased to 20 nm, the 1.54 μm emission is no longer observable. This observation indicates that the exciton recombination zone under a bias voltage of 12 V occurs within 20 nm.

From these EL measurements, one could also determine the distribution of the electrically-excited excitons. This is because of the following.

- At room temperature, no emission from the ligands was observed, therefore, the IR emissions from the RE ions can only be attributed to the exciton-harvesting processes by the ligands;

- b) In the absence of any energy offset between $\text{Nd}(\text{DBM})_3\text{bath}$ and $\text{Er}(\text{DBM})_3\text{bath}$ (since the ligands are the same), the IR emissions from the RE ions are not affected by any electron injection barrier;
- c) At these IR wavelengths, the visible emissions of the HT material (TPD) or the interface exciplex states will be absent. Without any overlapping spectra, the narrow emission peaks in the IR region are due to the carrier recombination within the entire ET layer.

As shown in Fig. 2 insert, we observed a dramatic decrease of the $1.54 \mu\text{m}$ emission of Er^{3+} ion with decreasing thickness of the $\text{Er}(\text{DBM})_3\text{bath}$ layer within the recombination zone. This suggests the possibility of a spaced electrical exciton distribution. As the occupation of the Nd complex was increased from 1 nm to 5 nm, the peak intensity of the $1.54 \mu\text{m}$ emission decreases by a factor of almost 20 times. However, when the Nd complex occupation was increased from 5 nm to 15 nm, the decrease in the $1.54 \mu\text{m}$ emission is much less compared to the former. This indicates that within the 20 nm recombination zone, the majority of the recombination takes place near the TPD/ $\text{Nd}(\text{DBM})_3\text{bath}$ organic interface. From the inset of Fig. 2, the spaced excitons at a fixed voltage do not display any linear separation. This clearly demonstrates the feasibility of modulating the infrared EL output of devices by means of configuring their active areas in a layered structure.

However, modulating the infrared emissions of one device electrically would be more practical and convenient for device applications. By applying different voltages, the exciton distribution within the recombination zone can be modulated to suppress one emission band over the other. In order to investigate the feasibility of electrically-modulated infrared emission, a layered device [TPD (60 nm)/ $\text{Nd}(\text{DBM})_3\text{bath}$ (5 nm)/ $\text{Er}(\text{DBM})_3\text{bath}$ (55 nm)/Mg:Ag (10:1, 150 nm)] was fabricated. Voltage-modulated infrared EL spectra are shown in Fig. 3. For clarity, the spectrum collected at the 6.5 V was smoothed to allow comparison with the EL spectra collected at higher voltages. All the spectra were normalized with respect to the $1.064 \mu\text{m}$ emission. When the voltage was increased to 18 V, the $1.54 \mu\text{m}$ emissions from the $\text{Er}(\text{DBM})_3\text{bath}$ is relatively weaker compared to that at 6.5 V. The normalized EL spectra show a voltage-dependent $1.54 \mu\text{m}$ emission.

It is important to note that both the Er and Nd complexes have the same ligands and only exhibit different central ion emissions. For a device with a 5 nm thick $\text{Nd}(\text{DBM})_3\text{bath}$ and 55 nm thick $\text{Er}(\text{DBM})_3\text{bath}$ layers, the ratio of infrared emissions provides a clear indication of the exciton distribution at the ligands under different voltages. Fig. 4 shows a plot of the intensity ratio of Er emission (at $1.54 \mu\text{m}$) to Nd emission (at $1.064 \mu\text{m}$) as a function of bias voltage. As the bias is increased, both the NIR emissions of the Nd and Er complexes increase, but the ratio between $1.54 \mu\text{m}$ and $1.064 \mu\text{m}$ emissions decrease by 36% (At 18 V, the intensity ratio was at 0.53, compared to the value of 0.82 at 6.5 V). This shows that for the device with a 5 nm thick $\text{Nd}(\text{DBM})_3\text{bath}$, there is an major increase in exciton

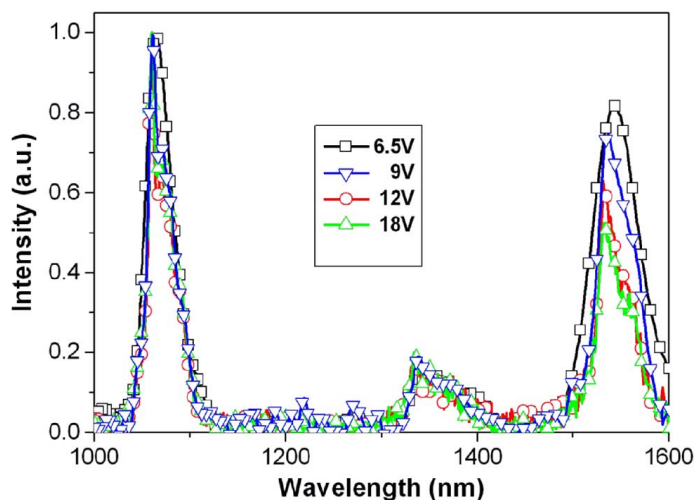


Fig. 3. The infrared EL spectra of OLED with structure: TPD (60 nm)/ $\text{Nd}(\text{DBM})_3\text{bath}$ (5 nm)/ $\text{Er}(\text{DBM})_3\text{bath}$ (55 nm)/Mg:Ag (10:1, 150 nm), at 6.5 V, 9 V, 12 V and 18 V. For clarity, the spectral collected at the reference voltage of 6.5 V was smoothed to allow comparison with the EL spectra collected at higher voltages.

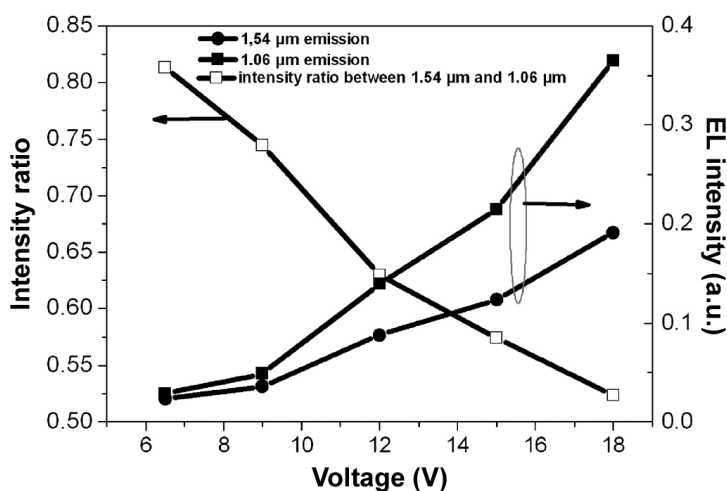


Fig. 4. A plot of $1.064 \mu\text{m}$ and $1.54 \mu\text{m}$ EL intensities versus voltage and the intensity ratio between $1.54 \mu\text{m}$ and $1.064 \mu\text{m}$ emissions

utilization as the number of charges are increased within the recombination zone.

In OLEDs, the exciton recombination zone and the charge distribution is highly dependent on the applied electric field (E) in devices. In most cases, due to the relatively lower electron mobility, the exciton recombination occurs mainly near the cathode at low bias voltage. When a higher E field is used, the mobility μ , follows the Poole-Frenkel relationship [14], $\mu_e \propto \exp(\beta\sqrt{E})$ where β is the Poole-Frenkel factor. By increasing E field, there will be a larger injected current which results in the enhanced filling of electron traps. Thus the electron mobility μ_e increases and this shifts the recombination zone to the anode and alters the exciton distribution.

With respect to the configuration for the 5 nm $\text{Nd}(\text{DBM})_3\text{bath}$ and 55 nm $\text{Er}(\text{DBM})_3\text{bath}$, the results

shown in Fig. 3 and Fig. 4 indicate that the exciton distribution in the recombination zone is non-linear and is highly dependent on the applied E field. The gradual decrease in the 1.54 μm emission also indicates that the exciton recombination zone has either shifted or shrunk. This result agrees well with other reports for both the visible small molecule and polymer systems [12], [15].

We have also attempted to improve on the IR EL modulation (i.e., to obtain greater contrast between the 1.064 μm and 1.54 μm as the voltage is varied) of these devices by modifying the energy offset by using different ligands [such as TPPO = tri-phenylphosphine oxide or ACA = tris-(acetylacetonato)]. However, their electrical properties and IR emission properties are not comparable with that of the (DBM)₃bath system. Further work on the use of suitable ligands to enhance the tunability and contrast between the different emission bands is needed; such ligands should exhibit good electron mobility and compatible T₁ energy level to facilitate the energy transfer to the rare-earth 4f infrared-emissive energy levels [16].

IV. CONCLUSION

In summary, we demonstrate the feasibility of modulated infrared emission from OLED based on RE complexes. This can be achieved by means of changing the configuration of the layers or by adjusting the operating voltage. Compared to inorganic counterparts [17], [18], these can be easily realized at room temperature. The exciton distribution in the recombination zone in the OLEDs could be affected by: (1) the proximity of the exciton distribution to the TPD/ Nd(DBM)₃bath organic interface and (2) the exciton formation ratio under the influence of different E fields. Such modulated infrared OLED devices could have future applications in multi channel wavelength-division multiplexing (MDW) communications.

REFERENCES

- [1] R. J. Curry and W. P. Gillin, "1.54 μm electroluminescence from erbium (III) tris(8-hydroxyquinoline) (ErQ)-based organic light-emitting diodes," *Appl. Phys. Lett.*, vol. 75, p. 1380, 1999.
- [2] H. Suzuki, "Infrared electroluminescence from an organic ionic dye containing no rare-earth ions," *Appl. Phys. Lett.*, vol. 80, p. 3256, 2002.
- [3] N. Tessler, V. Medvedev, M. Kazes, S. Kan, and U. Banin, "Efficient near-infrared polymer nanocrystal light-emitting diodes," *Science*, vol. 295, p. 1506, 2002.
- [4] C. Borek, K. Hanson, P. I. Djurovich, M. E. Thompson, K. Aznavour, R. Bau, Y. Sun, S. R. Forrest, J. Brooks, L. Michalski, and J. Brown, "Highly efficient, near-infrared electrophosphorescence from a Pt-metalloporphyrin complex," *Angew. Chem. Edit.*, vol. 46, p. 1109, 2007.
- [5] E. L. Williams, J. Li, and G. E. Jabbour, "Prediction of the thermal annealing of thick oxide metal-oxide-semiconductor dosimeters irradiated in a harsh radiation environment," *Appl. Phys. Lett.*, vol. 89, p. 083506, 2006.
- [6] Y. Kawamura, Y. Wada, Y. Hasegawa, M. Iwamuro, T. Kitamura, and S. Yanagida, "Observation of neodymium electroluminescence," *Appl. Phys. Lett.*, vol. 74, p. 3245, 1999.
- [7] Z. R. Hong, C. J. Liang, R. G. Li, F. X. Zang, D. Fan, and W. L. Li, "Infrared and visible emission from organic electroluminescent devices based on praseodymium complex," *Appl. Phys. Lett.*, vol. 79, p. 1942, 2001.
- [8] L. H. Slooff, A. Polman, F. Cacilli, R. H. Friend, G. A. Hebbink, F. C. J. M. van Veggel, and D. N. Reinhoudt, "Near-infrared electroluminescence of polymer light-emitting diodes doped with a lissamine-sensitized Nd³⁺ complex," *Appl. Phys. Lett.*, vol. 78, p. 2122, 2001.
- [9] Y. Yang and Q. Pei, "Voltage controlled two color light-emitting electrochemical cells," *Appl. Phys. Lett.*, vol. 68, p. 2708, 1996.
- [10] J. Kalinowski, P. Di Marco, M. Cocchi, V. Fattori, N. Camaioni, and J. Duff, "Voltage-tunable-color multilayer organic light emitting diode," *Appl. Phys. Lett.*, vol. 68, p. 2317, 1996.
- [11] P. E. Burrows, S. R. Forrest, S. P. Sibley, and M. E. Thompson, "Color-tunable organic light-emitting devices," *Appl. Phys. Lett.*, vol. 69, p. 2959, 1996.
- [12] F. X. Zang, Z. R. Hong, W. L. Li, M. T. Li, and X. Y. Sun, "1.4 μm band electroluminescence from organic light-emitting diodes based on thulium complexes," *Appl. Phys. Lett.*, vol. 84, p. 2679, 2004.
- [13] L. R. Melby, N. J. Rose, E. Abramson, and J. C. Caris, "Synthesis and fluorescence of some trivalent lanthanide complexes," *J. Am. Chem. Soc.*, vol. 86, p. 5117, 1964.
- [14] J. Kalinowski, L. C. Palilis, W. H. Kim, and Z. H. Kafafi, "Determination of the width of the carrier recombination zone in organic light-emitting diodes," *J. Appl. Phys.*, vol. 94, p. 7764, 2003.
- [15] P. W. M. Blom and M. J. M. De Jong, "Electrical characterization of polymer light-emitting diodes," *IEEE J. Sel. Topics Quantum Electron.*, vol. 4, p. 105, 1998.
- [16] T. S. Kang, B. S. Harrison, T. J. Foley, A. S. Kniefely, J. M. Boncella, J. R. Reynolds, and K. S. Schanze, "Near-infrared electroluminescence from lanthanide tetraphenylporphyrin: Polystyrene blends," *dv. Mater.*, vol. 15, p. 1093, 2003.
- [17] G. Scamarcio, F. Capasso, J. Faist, C. Sirtori, D. L. Sivco, A. L. Hutchinson, and A. Y. Cho, "Tunable interminiband infrared emission in superlattice electron transport," *Appl. Phys. Lett.*, vol. 70, p. 1796, 1997.
- [18] F. X. Zang, O. Lengyel, W. Li, Z. R. Hong, Z. Liu, C. S. Lee, and S. T. Lee, "Electron mobility of rare earth complexes measured by transient electroluminescence method," *Sol. Sta. Ele.*, vol. 50, p. 1584, 2006.

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