

Infrared organic light emitting diodes using neodymium *tris*-(8-hydroxyquinoline)

O. M. Khreis

Hijawi Faculty for Engineering and Technologies, Yarmouk University, Irbid, Jordan

R. J. Curry, M. Somerton, and W. P. Gillin

Department of Physics, Queen Mary and Westfield College, University of London, London E1 4NS, United Kingdom

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We have studied the photoluminescence and electroluminescence of neodymium *tris*-(8-hydroxyquinoline) and have found evidence, from the Stark splitting of the neodymium emission, for two isomers of the molecule. Following sublimation it appears that one of these isomers predominates. Photoluminescence can be excited through absorption into the organic ligands and there appears to be efficient coupling between the singlet and triplet exciton levels in the ligand and the internal levels of the neodymium. We can obtain bright infrared electroluminescence from the intraatomic levels within the neodymium at wavelengths of 900, 1064, and 1337 nm.

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INTRODUCTION

Near infrared luminescence from organic materials has been attracting interest recently due to the potential of producing electroluminescent devices on a range of substrates. Recent work has shown that electroluminescence can be obtained, at various wavelengths, from rare-earth containing organometallic compounds. For example, europium and terbium^{1,2} have been used to obtain sharp visible luminescence and neodymium and erbium to produce infrared luminescence.^{3,4} The potential for the infrared emitters include integrating the materials directly onto silicon to produce devices for interchip communications or in the case of erbium containing molecules for integrated 1.5 μm sources for telecommunications applications.⁴

In recent work we have shown that not only can we obtain 1.5 μm photoluminescence from erbium *tris*-(8-hydroxyquinoline) (ErQ),⁴ but we can also produce electroluminescent diodes grown on indium-tin-oxide (ITO) substrates using ErQ as the electron transporting and emitting layer and N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-3,3'-diamine (TPD) as the hole transporting layer.⁵ In this article we describe detailed photoluminescence and electroluminescence experiments on neodymium *tris*-(8-hydroxyquinoline).

EXPERIMENTAL METHOD

Neodymium *tris*-(8-hydroxyquinoline) was synthesized by dissolving neodymium chloride in de-ionized water and 8-hydroxyquinoline in an 80% methanol 20% de-ionized water solution. The first solution was slowly added to the second over a period of 2 h while undergoing stirring at ambient temperature. Further methanol was added and the solution left stirring overnight. The solution was then filtered and the remaining precipitate washed with methanol, at -25°C , to try to remove any remaining 8-hydroxyquinoline. The resulting substance was then dissolved in methanol at ambient

temperature and hexane was added until a fine precipitate was seen. The solution was then placed in a freezer to cool before the precipitate was finally collected. Liquid chromatography was then used to ascertain that only one material was present in the precipitate.

For the photoluminescence measurements either a 400 nm thick sublimed film or a quantity of the bulk powder in a quartz curvette was placed inside a continuous flow cryostat, which allowed the temperature to be varied between 4 and 300 K. Photoluminescence was excited using various lines from a UV enhanced argon ion laser, dispersed in a 1 m spectrometer and detected using an S-20 photomultiplier for the visible wavelengths or a liquid nitrogen cooled Ge detector for the infrared. All spectra were corrected for the response of the system. To obtain the absorption spectra 0.1 g of neodymium chloride was dissolved in 50 ml of methanol. The absorption spectra were obtained using an Hitachi U-3000 spectrophotometer.

All sublimed films and diodes were fabricated at a base pressure of $\sim 10^{-6}$ Torr. Diodes were formed on to cleaned ITO coated glass substrates and consisted of a 50 nm layer of TPD as a hole transporting layer followed by 60 nm of the NdQ, all deposited at 2–3 $\text{\AA}/\text{s}$. The top contact was a 200 nm layer of aluminum.

RESULTS AND DISCUSSION

A sample of the bulk powder was used to measure the visible, ligand related, photoluminescence using both 351 and 457 nm excitation wavelengths as a function of temperature. Figure 1 shows the 80 K photoluminescence for these two excitation lines along with the absorption curve for a solution of neodymium chloride in methanol. As the temperature is increased the shape of the photoluminescence does not significantly change, although the intensity of the photoluminescence reduces slightly; by approximately 10% for the 457 nm excitation and $\sim 30\%$ for the 351 nm excita-

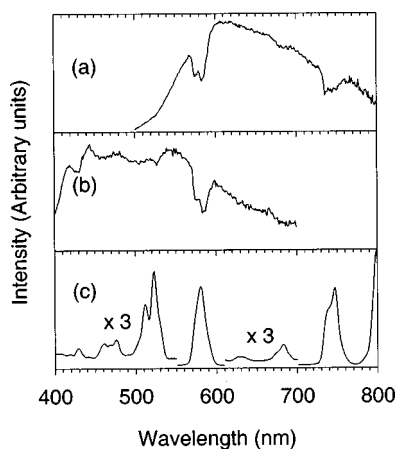


FIG. 1. The 80 K visible photoluminescence from bulk NdQ powder excited using the (a) 457 nm line and the (b) 351 nm line from an argon ion laser. (c) shows the absorption spectra for Nd^{3+} ions obtained from a solution of NdCl_3 in methanol.

tion. From the absorption spectra of NdQ, shown as an inset to Fig. 2, both of these excitation wavelengths are within the ligand absorption bands so it is reasonable to believe that the visible photoluminescence is originating from the ligands. The detailed fine peak structure visible in these spectra are, however, not characteristic of organic materials. By comparing the positions of the troughs in the visible photoluminescence with the peaks in the absorption of a NdCl_3 solution [Fig. 1(c)] we can ascribe these sharp features to absorption of the photoluminescence by the Nd^{3+} ions within the molecules. The presence of these absorption lines in the photoluminescence spectra again support our assumption that it is the ligand which is responsible for the broad visible photoluminescence.

It can be seen from Fig. 1 that there are significant differences between the visible photoluminescence excited using the two wavelengths. Although absolute peak positions for the emission cannot be determined, due to the presence of the absorption lines, it appears that the photoluminescence peak for the 351 nm excited sample is $\sim 450\text{--}550$ nm, whereas for the 457 nm excited luminescence the peak is at $\sim 600\text{--}650$ nm. These results are in qualitative agreement with results we have obtained for AIQ.⁶ In that work we investigated the luminescence of AIQ as a function of excitation wavelength and temperature and noted dramatic shifts

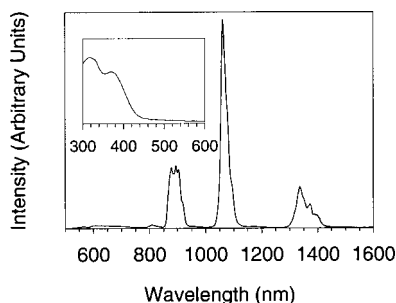


FIG. 2. The 80 K photoluminescence from bulk NdQ powder excited at 457 nm. The spectra has been corrected for the response of the system. The inset shows the absorption spectra for NdG.

in the photoluminescence spectra. These shifts were attributed to longer wavelength excitations being directly absorbed to form triplet excitons, some of which could radiatively recombine giving photoluminescence at ~ 600 nm. We also noted that the long wavelength tail observed in the UV excited photoluminescence of AIQ but not in the electroluminescence could be attributed to triplet exciton recombination.

If the highest occupied molecular orbital to lowest unoccupied molecular orbital separation is not strongly modified by the central ion we would expect NdQ to give a roughly similar visible luminescence to AIQ. However, even ignoring the effects of the absorption lines, the UV excited NdQ photoluminescence appears to be much broader than that for AIQ. This broadening could be attributed to greater radiative recombination of triplets, which could be caused by the greater spin-orbit interaction caused by the larger mass of Nd compared to Al. These triplets, having a lower energy than the singlet excitons, would result in emission in the tail of the singlet spectra and hence the observed broadening.

For the 457 nm excitation the shift in the photoluminescence peak is very much more pronounced than in AIQ. From the photoluminescence there appears to be almost no singlet recombination visible, the ~ 500 nm peak, and very little dependence of either peak position or intensity with temperature, $\sim 10\%$ increase in intensity between 300 and 80 K.

It should be stressed that independent of excitation wavelength the visible photoluminescence from this material is exceptionally weak (~ 1 in 10^3) when compared to AIQ measured under identical conditions.

Figure 2 shows the photoluminescence of bulk NdQ recorded from 500 nm to $1.6\ \mu\text{m}$ using 100 mW of 457 nm excitation. This figure is a composite of the visible range collected using the photomultiplier and the infrared range collected using the Ge detector. The spectra have been scaled to match where they overlap to demonstrate the relative intensities of the two regions. From Fig. it can be seen that, compared to the weak visible luminescence, there are three strong infrared emission lines centred at ~ 900 , 1064, and 1337 nm which correspond to the ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$, ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$, and ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$ transitions, respectively. The observation of this very strong luminescence from the intra-atomic neodymium levels coupled with very weak luminescence from the organic ligands suggests very efficient energy coupling between the ligands and the ion. This is supported by the observation of Nd absorption lines in the ligand luminescence, which show that the singlet and triplet levels in the ligands are resonant with levels within the Nd^{3+} ion.

Figures 3 and 4 show detailed low temperature luminescence spectra for the ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ and ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transitions, respectively, recorded from both bulk NdQ powder and from 400 nm films of sublimed NdQ. Figure 3 shows the 5 K spectra from the ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition, for the bulk powder and ten peaks can be clearly resolved. These peaks are due to the Stark splitting of the ${}^4I_{9/2}$ level due to the local electric field seen by the Nd atom. NdQ would be expected to form two isomers, fac and mer, which would have C_3 and C_1 symmetry respectively. These two isomers would leave

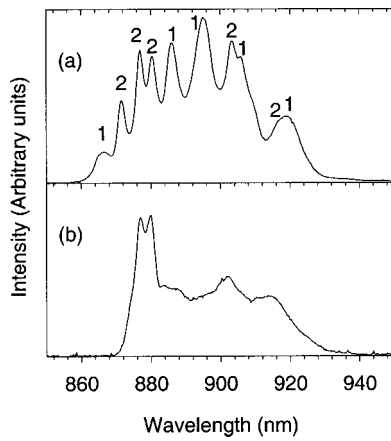


FIG. 3. The 5 K photoluminescence from the ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition within the Nd^{3+} ion for: (a) bulk NdQ and (b) a 400 nm sublimed film. The peaks marked 1 and 2 in (a) are believed to be due to the different isomers with 2 being the predominant peaks in the sublimed film.

the Nd^{3+} ion in sites of C_3 or C_1 symmetry. For the ${}^4I_{9/2}$ level both of these site symmetries would result in the Stark splitting producing five levels, so the presence of ten peaks in the bulk NdQ spectrum would suggest that the powder is a mixture of the two isomers. For the sublimed film it is only possible to clearly resolve five peaks, although there is probably some contribution to the background from at least one of the other peaks, which suggests that this layer may consist of mainly one isomer. Although these results appear to show that mainly one isomer is present in the sublimed films, we are not able to detect which of the two isomers it is. It is also not clear what the mechanism resulting in the deposition of a single isomer during evaporation is. It could be that the two isomers have very different sublimation temperatures, causing one to sublime preferentially or it may be that one of the isomers can be transformed with temperature, however, this will need further study. For the ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition the difference is not as clear (Fig. 4). For this level, due to the Stark splitting, we should see six transitions for each isomer. However, for the bulk NdQ sample we only observe, at most, eight peaks and at least five of these are also present in the sublimed film. While some of the transitions present in the

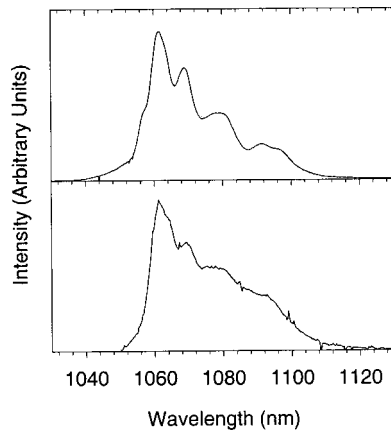


FIG. 4. The 5 K photoluminescence from the ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition within the Nd^{3+} ion for: (a) bulk NdQ and (b) a 400 nm sublimed film.

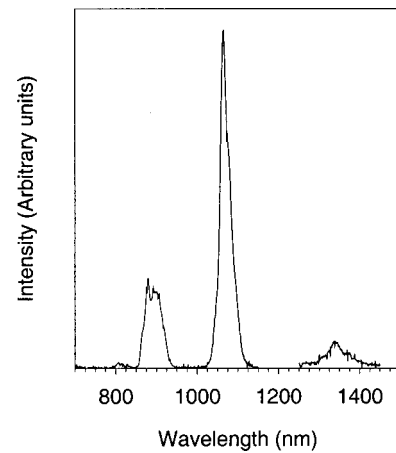


FIG. 5. The 300 K electroluminescence from a ITO/TPD/NdQ/Al diode.

bulk powder are not present in the sublimed film and are probably due to the second isomer we suggest that some of the detail is hidden due to the high intensity of these levels, which is resulting in them being quite broad. It should also be noted that the positions of the peaks need not necessarily be different for the two isomers and this may be an additional factor in the splitting not being as clear for this level as for the ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition.

Figure 5 shows the infrared electroluminescence obtained from an ITO/TPD/NdQ/Al diode at an operating voltage of 30 V, which corresponded to a current through the diode of 78 mA/cm^2 . This diode showed no visible electroluminescence but strong infrared luminescence centred at $\sim 900, 1060,$ and 1320 nm as seen in the photoluminescence. As the electroluminescence spectra were recorded at 300 K, the peaks are therefore somewhat broader than for the spectra shown in Fig. 3 and 4. However, close investigation of the ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition shows that it looks more like the photoluminescence of the sublimed film as opposed to the bulk powder with a number of the peaks being less clearly resolved. This is not surprising in light of our explanation of the differences in the photoluminescence between the sublimed films and the bulk powder. Figure 6 shows the intensity of the electroluminescence, at 1064 nm, as a function of the current density through the diode. It can be clearly seen that the diodes start emitting at a current density of ~ 0.23

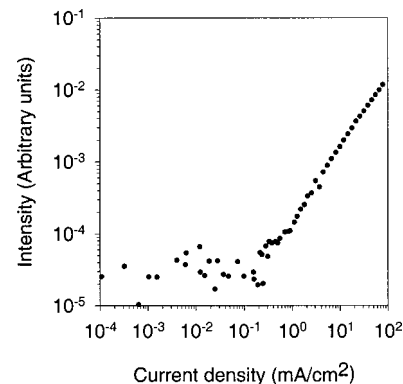


FIG. 6. The electroluminescence intensity at 1064 nm as a function of the current density through the diode.

mA/cm², which corresponds to a drive voltage of ~ 13 V. It can also be seen that once the diodes switch on there is a linear increase in intensity with current through the diodes. The current–voltage (I – V) characteristics of these diodes showed a turn on voltage in forward bias of ~ 13 V and no breakdown in reverse bias up to voltages of -30 V. While the 13 V turn on voltage is quite high, we have made no attempt to optimize these diodes, through oxygen plasma treatment of the ITO or using low work function metals and we see no fundamental reasons why this could not be reduced in the future.

CONCLUSIONS

In conclusion we have studied the photoluminescence of neodymium *tris*-(8-hydroxyquinoline) and have found evidence, from the Stark splitting of the neodymium emission,

for two isomers of the molecule. Following sublimation it appears that one of these isomers predominates. Photoluminescence can be excited through absorption into the organic ligands and there appears to be efficient coupling between the singlet and triplet exciton levels in the ligand and the internal levels of the neodymium. We can obtain bright infrared electroluminescence from the intra-atomic levels within the neodymium.

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