Near Infrared Electroluminescence from Nd(TTA)₃Phen in Solution-Processed Small Molecule Organic Light Emitting Diodes

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Abstract

We report on the near infrared electroluminescence properties of a Nd^{3+} complex with thenoyltrifluoroacetone and 1,10-phenantroline ligands in solution-processed organic light-emitting diodes. Spin-coated blends containing a 1,3-bis(9-carbazolyl)benzene host doped with the Nd^{3+} complex were found to exhibit a photoluminescence quantum yield of about 0.5%, regardless of the doping concentration level. Electroluminescent devices based on these small molecule blends showed the characteristic emission of Nd^{3+} at 890, 1060 and 1330 nm with an external quantum efficiency as high as 0.022%. These improved performances were mainly attributed to direct charge trapping and exciton formation on the near-infrared emitter. Importantly, the efficiency roll-off at high current densities due to triplet-triplet exciton annihilation in the device containing 20 wt.% of the complex was lower than what is typically observed in lanthanide complex-based electroluminescent devices. This is presumably due to the high triplet energy of the host material, which prevents guest-to-host energy-back transfer and thus host-guest triplet-triplet exciton annihilation.

Keywords: solution-processed OLEDs; small molecule host; near infrared electroluminescence; neodymium complex; efficiency roll-off.

1. Introduction

In recent decades, luminescent lanthanides have attracted a tremendous amount of interest due to their potential applications in optoelectronics, sensors, and luminescent probes [1, 2, 3]. In particular, thanks to their long excited state lifetimes and narrow-band emission, they are widely used in optically-pumped plastic lasers and amplifiers [4], and are also promising candidates for the realization of organic semiconductor laser diodes [5]. Furthermore, amongst all the lanthanide ions, Nd^{3+} , Er^{3+} , Pr^{3+} , Tm^{3+} and Yb^{3+} are emissive in the near infrared (NIR) region at some important wavelengths in the range of 900-1600 nm, making them attractive candidates for optical telecommunication applications [6]. To this end, lanthanide based near infrared organic light emitting diodes (NIR-OLEDs) would be promising devices for realizing electrically-pumped organic light sources [7].

In the past, Nd^{3+} based OLEDs have been fabricated by incorporating Nd^{3+} complexes into conventional conjugated polymers by solution-processing [8, 9, 10], and also by thermal evaporation technique in non-doped structures [11, 12, 13, 14]. Compared with thermal deposition method, solution-processing is a more demanding technique for large-area manufacturing purposes. Solution-processing is also economically a more attractive method in terms of minimized material usage and its compatibility with some inexpensive manufacturing techniques such as spin-coating, ink-jet printing, and screen-printing processes [15]. In addition, solution-processing seems to be more appropriate for incorporating lanthanide complexes into host materials in terms of thermal and electrical stability. For example, Sano and Hamada reported a poor thermal stability for $\text{Eu}(\text{TTA})_3$ at the temperatures required for evaporation [16].

Although some solution-processed Nd^{3+} based OLEDs with polymeric hosts have been reported before [8, 9, 10], to the best of our knowledge, solution-processed Nd^{3+} based NIR

OLEDs using small molecule hosts have not been reported so far. Noticeably, 1,3-bis(9-carbazolyl)benzene (mCP) is a commonly used thermal and solution-processable material which has a triplet excited state energy of 2.9 eV, making it a very suitable host material, especially, in phosphorescent OLEDs due to the reduced energy-back transfer from the emitters to mCP [17, 18, 19, 20]. In this study, OLEDs based on blends containing a mCP host doped with NIR emitting Nd(TTA)₃phen, (TTA=thenoyltrifluoroacetone, phen=1,10-phenanthroline) were fabricated. The triplet energy of mCP was high enough to sensitize the Nd³⁺ complex, yielding a maximum electroluminescence (EL) external quantum efficiency (EQE) as high as 0.022% for the device containing 20 wt.% of the NIR emitter. This EQE value is higher than the reported values for solution-processed Nd³⁺ based polymer OLEDs [9, 10]. Further, no emission from mCP was detected in this device. More importantly, in comparison to the previously reported NIR-OLEDs based on Nd³⁺ complexes, this device suffers less from triplet-triplet (T-T) annihilation processes at high current densities, which are believed to be the most detrimental processes for the realization of electrically-driven organic lasers based on lanthanide complexes.

Experimental details

2-1 Materials and electrochemical measurements

The chemical structures of the compounds used in this study are depicted in **Fig. 1**. The NIR emitter, Nd(TTA)₃phen, was synthesized using the conventional method [21]. The lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energy levels of Nd(TTA)₃phen were determined by electrochemical measurements. For this purpose, all cyclic and differential-pulse voltammetry were carried out in dimethylformamide (DMF) containing 0.1 M *n*Bu₄NPF₆ with the three electrodes system using glassy carbon working, Pt wire

counter and Ag/Ag⁺ reference electrodes. The electrochemical potential was calibrated using the ferrocene/ferrocenium (Fc/Fc⁺) couple as an external standard.

2.2. Device fabrication and characterizations

Four NIR-OLEDs were fabricated on pre-patterned 100 nm thick indium tin oxide (ITO)-coated glass substrates (Atsugi Micro Co.) by sequential depositing the organic layers using solution and evaporation techniques. The ITO substrate had a sheet resistance of 25 Ω /sq. The substrates were cleaned with detergent, 2-propanol, acetone, and isopropyl alcohol in an ultrasonic bath for 10 min each and then dried with nitrogen. Next, the substrates were UV-ozone treated for 15 min. The structures of the four different OLEDs are the followings: ITO/PEDOT:PSS/mCP:Nd(TTA)₃phen (x=7, 13, 16, and 20 wt%)/TPBi/LiF/Al, where x represents the concentration of Nd(TTA)₃phen in the mCP host. To fabricate these devices, a 30 nm thick layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Clevios Al 4083, Heraeus) was first spin-coated onto the pre-cleaned ITO substrates and then baked at 140 °C for 20 minutes. Next, the active layers containing different concentrations of the NIR emitter doped in mCP (JIDA OPTOELECTRONICS) were spin-coated onto the PEDOT:PSS layer from chloroform at a concentration of 10 mg/ml. The measured average thicknesses of these active layers were about 60 nm. Note that the deposition of the active layers was carried out in a nitrogen-filled glove box. After that, a 40 nm thick layer of electron transporting 2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole), TPBi (JIDA OPTOELECTRONICS) was thermally deposited onto the emission layers at an evaporation rate of 0.1 nm/s under a vacuum of < 10⁻⁴ Pa. The cathode was then fabricated by thermal evaporation of a 0.8 nm thick LiF followed by a ~100 nm thick Al layer with an evaporation rate of 0.01 nm/s for LiF and 0.3 nm/s for Al. The active area of the devices was 4 mm². The devices were finally encapsulated with a

commercially available ultraviolet curing epoxy resin and glass coverslips in a glove box. For convenience, we hereafter call the devices containing 7, 13, 16, and 20 wt% of Nd(TTA)₃phen device A, B, C, and D, respectively. It should be noted that attempts to prepare devices with higher Nd³⁺ concentrations failed due to the limited solubility of the lanthanide complex in chloroform.

The current density-voltage (J-V) characteristics and EQE measurements were carried out using a semiconductor parameter analyzer (E5273A, Agilent) connected to an optical power meter (1936-C, Newport) and an InGaAs photodetector (918D, Newport) with the spectral range of 800-1650 nm in the ambient atmosphere. Assuming a Lambertian emission profile for the NIR emitted light in the forward direction, the EQEs of the NIR-OLEDs were calculated using the procedure employed in [22]. The EL spectra of the OLEDs in the visible region were measured using an optical fiber connected to a spectrometer (PMA-12, Hamamatsu Photonics). The EL spectra of the devices in the NIR region were recorded using a NIR spectrometer (C11482GA, Hamamatsu Photonics).

The absorption spectrum of Nd(TTA)₃phen was recorded using a UV-visible spectrophotometer (UV-2550, Shimadzu). The steady-state photoluminescence (PL) spectrum of mCP in the visible region was recorded by a spectrofluorometer (Fluoromax-4, Horiba Jobin Yvon). The PL quantum yields (PLQYs) of the mCP:Nd(TTA)₃phen blended films for different doping concentrations were recorded using a UV-NIR PLQY measurement system (C13534, Hamamatsu). The PLQY measurement for the neat mCP film was recorded using an absolute PLQY spectrometer (C11347 Quantaurus-QY, Hamamatsu). The NIR PL spectrum was measured by exciting the sample with a nitrogen laser ($\lambda = 337$ nm, repetition rate of 8 Hz, pulse width of 800 ps). The Atomic Force Microscope (AFM) images of the solution-processed films were recorded by JEOL (JSPM-5400 model) scanning probe microscope. It is important to note that the

organic thin films prepared for the photophysical and AFM measurements were spin-coated on top of pre-cleaned fused silica substrates.

3. Results and discussions

3.1. Electrochemical measurements

Figure 2 shows cyclic and differential-pulse voltammograms of Nd(TTA)₃phen in DMF solution. Since the cyclic voltammograms (CV) of the complex was observed as irreversible waves, the HOMO and LUMO levels were solely determined employing the differential-pulse voltammograms, yielding the first oxidation and reduction potentials, noted E_{ox}^0 and E_{red}^0 . The HOMO and LUMO energy values were respectively calculated using the following equations: [23, 24]

$$\text{HOMO (eV)} = -1.4 E_{ox}^0 \text{ (vs. Fc/Fc}^+) - 4.6 \quad (1)$$

$$\text{LUMO (eV)} = -1.19 E_{red}^0 \text{ (vs. Fc/Fc}^+) - 4.78 \quad (2)$$

The use of these two equations leads to HOMO and LUMO energies of -5.4 eV and -2.5 eV, respectively, as indicated in **Fig. 1**. The measurement uncertainties for the HOMO and LUMO levels are evaluated to be 0.18 and 0.2 eV, respectively [23, 24]. According to these results, the electronic energy gap of the complex is calculated to be 2.9 eV.

3.2 Photophysical characterization

In Nd³⁺ complex based OLEDs, the Nd³⁺ ions can be excited *via* two mechanisms [2, 25]: i) excitons can be directly formed on the complex through injection of electrons and holes into the ligands, and then the Nd³⁺ ions can be sensitized through antennae effect *via* the triplet excited states of the complex, ii) singlet and triplet excitons can also be formed on the host molecules and then the singlet and triplet energies can be non-radiatively transferred respectively *via* Förster and Dexter-type energy transfer mechanisms from the host to the ligands followed by the energy

transfer to the Nd^{3+} ions from the ligands. It is noteworthy that efficient long-range Förster-type energy transfer mechanism from the host to the guest in a host-guest system requires a considerable overlap between the absorption spectrum of the guest and the emission spectrum of the host. **Figure 3** shows the steady-state PL spectrum of a mCP neat film and the absorption spectrum of the $\text{Nd}(\text{TTA})_3\text{phen}$ in dichloromethane. The mCP film exhibits the expected blue fluorescence with a maximum emission wavelength at 395 nm and a PLQY of 14.5 %. The Nd^{3+} complex shows some absorption features in the UV region, which are attributed to the absorption of the ligands. In particular, the peak centered at around 345 nm is due to the absorption of the TTA ligands. It is worth noting that the optical energy gap of the NIR complex is around 3.2 eV, which is in good consistency with the electronic energy gap measured by electrochemistry. More importantly, a spectral overlap around 350~400 nm can be seen between the absorption and the emission spectra displayed in **Fig. 3a**, indicating that Förster-type energy transfer should take place from the mCP host to the TTA ligands of the Nd^{3+} complex. **Table 1** shows the singlet and triplet energy levels of mCP and $\text{Nd}(\text{TTA})_3\text{phen}$ previously reported in the literature [26,27] whereas **Fig. 4** depicts the various sensitization pathways to the Nd^{3+} ion. Looking at the triplet energy values in this system, a sensitization of the dopant molecules through a Dexter-type energy transfer of the triplets from the mCP host to the ligands cannot be excluded. It can also be already stated that triplet excitons formed onto the organic ligands are well confined to the NIR emitting complexes due to the much larger triplet energy of the mCP host. For instance, Steemers et al. [28] demonstrated that when the gap between the organic ligands and the $\text{Ln}(\text{III})$ is larger than 2000 cm^{-1} (corresponding to a gap of nearly 0.25 eV), no significant back energy transfer could occur. Based on this previous study and the values of the triplet energies provided in **Table 1**, we can exclude back energy transfer to occur from the Nd complex to the mCP host.

An example of NIR PL spectrum from a mCP:Nd(TTA)₃phen (16 wt.%) blended film is given in **Fig. 3b**. This representative sample showed the characteristic emission of Nd³⁺ with three peaks at 890 nm ($^4F_{3/2} \rightarrow ^4I_{9/2}$), 1060 nm ($^4F_{3/2} \rightarrow ^4I_{11/2}$), and 1330 nm ($^4F_{3/2} \rightarrow ^4I_{13/2}$). To gain further insights into the photophysical properties of these mCP: Nd(TTA)₃phen blends, PLQY of the NIR emission from the Nd³⁺ complex and PLQY of visible emission from the mCP host were measured as a function of the doping concentration. For this purpose, the blends A, B, C and D (corresponding to concentrations of the Nd(TTA)₃phen equal to 7, 13, 16, and 20 wt%, respectively) were photo-excited at 345 nm where both mCP host and the TTA ligands strongly absorb light. The PLQY values for the NIR emission were measured to be 0.4 % for the blend A and 0.5 % for the three other doped films. These similar values, which are in the range of the experimental uncertainties, indicate that the effect of the doping concentration on the NIR emission efficiency is nearly the same for this range of doping concentration. Noticeably, the doping concentration was found to have a much more significant impact on the PLQY of the mCP blue emission. These PLQY values were measured to be 0.5, 0.3, 0.1 and around 0 % for the blends A, B, C and D, respectively, which is significantly lower than the value obtained in an mCP neat film. The results provide clear evidence of an increase of the mCP emission when the concentration of NIR emitters is decreased. This suggests that the Förster-type energy transfer taking place in these blends from mCP to Nd(TTA)₃phen is not efficient enough at low doping concentration. To gain additional insights into the energy transfer process, it should be noted that we also tried to examine the influence of the doping concentration on the PL decays of the mCP host emission in the blends. While the mCP neat film showed a PL lifetime of about 3.1 ns, the PL decays of the blends were too fast to be properly recorded using our experimental setup. This observation is consistent with a quenching of the host emission due to energy transfer. To the best of our knowledge, no PLQY

value for Nd^{3+} based guest-host systems has been reported in literature for the sake of comparison. Interestingly, according to the PLQY values measured above and assuming that both singlet and triplet excitons are involved in the electrical excitation of Nd^{3+} ions, it is worth noting that the theoretical maximum EQE value for OLEDs based on these blends is calculated to be around 0.1% with the assumption of both singlet and triplet harvesting under electrical excitation.

3.3 Characterization of the blend surface morphology by AFM measurements

Previous works have highlighted the importance of having a low surface roughness of the light-emitting layer for achieving high EQE values in OLEDs [29,30]. This surface roughness should be minimized to prevent current leakage and guarantee a stable film morphology upon thermal annealing [31]. In the case of spin-coated light-emitting layers, the selection of the host material is also of great importance since it must possess, in addition to the appropriate semiconducting properties, a good solubility in common organic solvents and a high thermal stability under annealing to prevent crystallization [31,32]. Even though mCP is highly soluble in chloroform, it tends to crystallize easily upon thermal annealing, exhibiting a hill-like surface morphology [32]. In that context, we characterized the surface morphologies of the blends A, B, C and D using AFM. As shown in **Fig. 5**, the root-mean-square (RMS) roughness values of the blend films were measured to be lower than 1 nm, indicating that the surface roughness should not affect significantly the OLED performances. It is also important to note that these AFM images did not show any clear signs of a phase separation between the host and guest molecules, suggesting a good and homogeneous dispersion of the Nd^{3+} complex in the mCP host.

3.4 Electroluminescence spectra of the NIR-OLEDs

The EL spectra of mCP and Nd(TTA)₃phen complex for device A at different driving voltages are shown in **Fig. 6**. This device emits light in the visible and NIR regions through injection of electrons and holes into the emission layer followed by the formation and recombination of excitons on both mCP and Nd(TTA)₃phen molecules. Observation of the visible emission from mCP indicates that the Förster-type energy transfer mechanism from the host molecules to the dopant molecules is not efficient enough to quench the emission of the host material at the 7 wt% doping concentration. This statement is fully supported by the PLQY measurements described above, which indicated a partial energy transfer for such a low dye concentration. As a consequence, we attribute most of the emission from this device to the direct exciton formation on the Nd(TTA)₃phen molecules. This interpretation is in good consistency with the low energy barriers for electron and hole injection respectively from TPBi and PEDOT:PSS to the LUMO and HOMO levels of the Nd(TTA)₃phen molecules.

Figures 7, 8 and 9 show representative EL spectra measured in devices B, C, and D, respectively. Similarly to device A, the three OLEDs are found to strongly emit in the NIR region with the characteristic emission spectrum from Nd³⁺. More importantly, these EL spectra show a gradual decrease of the mCP host emission intensity as the concentration of Nd(TTA)₃phen molecules is increased. This is consistent with the PLQY results and can be explained by the improvement of the Förster-type energy transfer from the host to the guest molecules when increasing the density of emitters. When looking at the energy levels of the different molecules used in the devices in **Fig. 1**, it can be seen that the HOMO and LUMO of Nd(TTA)₃phen are located within the HOMO and LUMO levels of mCP and that the LUMO of TPBi is close to that of Nd(TTA)₃phen. This suggests that holes and electrons can be directly trapped on the NIR emitters. In that case, by increasing the concentration of NIR emitters in the blend, most of the

charge carriers can be directly injected into the organic ligands, thus favoring direct exciton formation on the Nd^{3+} complex. For instance, in the case of device D, the EL from the mCP host is completely quenched, which is presumably due to both the improved direct exciton formation on $\text{Nd}(\text{TTA})_3\text{phen}$ and a more efficient energy transfer from the host to the guest emitters.

The NIR emission from $\text{Nd}(\text{TTA})_3\text{phen}$ for all the devices was very stable under electrical excitation but the blue emission from mCP was very unstable even under low and moderate driving voltages, making recording the EL spectra of mCP difficult. For example, this can be seen for the decreased mCP EL emission at the driving voltage of 16 V in **Fig. 8**. Since the devices were carefully encapsulated before device characterization, the emission instability of the host is presumably due to intrinsic degradation mechanisms [33]. Such an effect would adversely affect the host rather than the Nd^{3+} complexes, which are effectively protected by the ligands from their surrounding environment.

3.5 Electrical and efficiency characterization of the NIR-OLEDs

The current density-voltage (J-V) curves of the devices A, B, C and D are displayed in **Fig. 10a**. Devices A, B, and C started emitting light at about 9 V but the turn-on voltage increased up to 12.6 V in device D. These turn-on voltages are lower than the ones reported in the literature for Nd^{3+} complex based OLEDs, which are in the range of 12 to 30 V [8, 9, 10, 11, 13]. The results in **Fig. 10a** show a slight shift of the J-V curves with an increase of the doping concentration from 7 to 20 wt%, confirming that direct charge trapping on the emitters [34] is indeed a mechanism, which could take place in the devices in addition to the energy transfer from the host to the guest molecules. Noticeably, the 7 wt.% device showed the highest current densities while the 13 wt.% showed the worst J-V characteristics. A possible scenario to explain the observed behavior is the

following. In the 7 wt.% device, charge carriers are mainly transported by the mCP host and there is no significant charge trapping by the guest molecules. In that blend, energy transfer from the host to the guest molecules is presumably the dominant mechanism for exciton formation on the guest molecules. In the 13 wt.% device, charge carriers are partly trapped by the guest molecules while dopant molecules in the 16 wt.% and 20 wt.% OLEDs may form a channel for carrier transport. The EQE was measured as a function of the current density in devices A, B, C, and D. Because the electroluminescence of devices A, B and C is composed of both blue emission from the mCP host and NIR emission from the Nd³⁺ complex, only the data obtained in device D are plotted in **Fig. 10b**. As shown above, the electroluminescence in device D is indeed only composed of the NIR emission. The average maximum EQE value of five devices D is found to be around 0.022%. Even though the average maximum EQE values measured in devices A, B and C are 0.016 %, 0.020 % and 0.021 %, respectively, they contain certain amount of host emission and device D showed the highest efficiency from Nd³⁺. Noticeably, the maximum EQE value of device D is significantly higher than the best values reported in solution-processed Nd³⁺ based polymer OLEDs (0.001 and 0.007 %) [9, 10] and is comparable with the best values reported in thermally-evaporated devices (0.01 and 0.02 %) [22]. In particular, if we compare our results with those previously obtained using poly(N-vinylcarbazole) (PVK) as host [9,10], the device performance achieved in the present work can be explained by the use of TPBi for the electron transport layer and the better charge transport properties of the mCP host. While the electron and hole mobilities of mCP have been reported to be 3.4×10^{-5} and 1.2×10^{-4} cm²/Vs, respectively [35], hole mobility in PVK is 1×10^{-6} cm²/Vs [36]. Although mCP appears as a more appropriate host material than PVK for Nd(TTA)₃phen-based OLEDs, it should be mentioned that the highest EQE value achieved in this work is still lower than the theoretical maximum EQE value of 0.1%, suggesting

that an optimization of the device architecture should be possible to improve the charge balance and the overall performance of the Nd(TTA)₃phen-based devices.

As shown in **Fig. 10**, device D exhibits a low efficiency roll-off at high current densities. For instance, while the maximum measured EQE was 0.022%, the value at a current density of 700 mA/cm² decreased to 0.014%, which is still higher than half of the maximum efficiency (i.e. 0.011%). Based on previous studies devoted to lanthanide OLEDs, such an efficiency roll-off is attributed to triplet-triplet exciton (T-T) annihilation [37,38]. This process can occur between host molecules, between guest molecules, and also between host and guest molecules [38]. Adachi *et al.* [39] demonstrated that T-T annihilation between TTA ligand and CBP host in a CBP:Eu(TTA)₃phen system strongly lowered the efficiencies of their devices even under very low current densities. This was mainly due to the low triplet energy difference between CBP and TTA ligand (*i.e.* 0.13 eV), resulting in a strong energy-back transfer from TTA to CBP. Such a severe efficiency roll-off with CBP host and some other host materials with low triplet energy levels can also be found for lanthanide based OLEDs in the literature [40-44]. In contrast, as already mentioned, the energy differences between the triplet level of mCP and those of TTA and phen ligands are 0.55 eV and 1 eV, respectively. This implies a negligible energy-back transfer from the ligands to mCP due to the large triplet-triplet energy difference, preventing the host-guest T-T annihilation process to take place in this system. In addition, as mentioned before, when the gap between the organic ligands and the Ln(III) is larger than 2000 cm⁻¹ (corresponding to a gap of nearly 0.25 eV), no significant back energy transfer could occur [28]. Adachi *et al.* [39] also showed that T-T annihilation between two TTA ligands on the same Eu(TTA)₃phen complex (after triplet migration from CBP to TTA) is least likely possible due to the low concentration of Eu(TTA)₃phen (2 wt%) in their system. In the present study, this latter mechanism can presumably

occur because of the higher concentration of Nd³⁺ complex (20 wt.%). It is also not possible to fully exclude at the current stage the third T-T annihilation process, which is related to triplet exciton migration between mCP host molecules. In that context, we attribute the low efficiency roll-off observed in device D at high current densities to a significant reduction of the host-guest T-T annihilation process.

Overall, the best NIR-OLED based on Nd³⁺ complex fabricated in this study shows an improved maximum EQE value and a low efficiency roll-off at high current densities. Such an achievement could be obtained due to the direct formation of excitons on the NIR emitters, the improvement of the energy transfer from host to guest molecules by increasing the doping concentration up to 20 wt.%, and the selection of a host material with high T₁ energy, preventing back energy transfer from guest to host molecules and strongly reducing quenching by T-T annihilation. While these results are extremely promising for the possible use of these lanthanide complexes for electrically-pumped light sources, their performance still needs to be enhanced further to develop practical applications. To this end, further works should focus on (i) the improvement of the energy transfer from the host to the ligands of the Nd³⁺ complex while keeping an appropriate energy level alignment between HOMO and LUMO of the ligands and those of the host material for an efficient charge injection into the ligands, (ii) the use of fluorinated/deuterated host molecules and organic ligands to reduce the absorption of the NIR emission by the highly oscillating C-H and O-H bonds, and (iii) the replacement of ITO by another electrode material more transparent in the NIR region of the electromagnetic spectrum.

4. Conclusion

In summary, we demonstrated the first solution-processed small molecule NIR Nd³⁺ based OLEDs. Upon doping a mCP host with relatively large amounts of Nd(TTA)₃phen up to 20 wt.%,

the NIR devices exhibited higher EQE in comparison to the previously reported values in the literature. The main reasons for the improved performances obtained in the present work were direct charge trapping and formation of excitons on the Nd(TTA)₃phen NIR emitters, together with a partial energy transfer from the host material to the emitter, which was improved by increasing the doping concentration up to 20 wt.%. Moreover, the EQE of the best device showed a low efficiency-roll off at high current densities, most likely due to the large energy gap between the triplet energy levels of the ligands and that of mCP, resulting in a negligible energy-back transfer from the triplet excited states of the ligands to the triplet excited state of mCP. However, this efficiency roll-off presumably due to T-T annihilation on the ligands still needs to be reduced for practical applications. Overall, we believe that this study should greatly contribute in the near future to the development of high performance NIR-OLEDs based on Nd³⁺ complexes.

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Figure 1: Energy level alignments and chemical structures of the materials used in this study

Figure 2: (a) Cyclic and (b) differential-pulse voltammograms of Nd(TTA)₃phen in DMF. The initial potential of all voltammograms is 0 V (vs. Fc/Fc^+). The first oxidation and reduction potentials of Nd(TTA)₃phen are estimated to be 0.59 and -1.92 V (vs. Fc/Fc^+) from the peak potential in the differential-pulse voltammograms, respectively.

a

b

Figure 3: (a) Absorption spectrum of Nd(TTA)₃phen in 1mM dichloromethane (DCM) solution, and steady-state PL spectrum of mCP neat film. (b) PL spectrum from Nd(TTA)₃phen (16 wt.%) in mCP host using an excitation wavelength of 337 nm.

Figure 4: Energy diagram of the molecular system used in this work. The first excited singlet (S₁) and triplet (T₁) state energies of mCP and Nd(TTA)₃phen are indicated. ISC corresponds to intersystem crossing. The forbidden f-f transitions of the lanthanide ion are shown with dashed arrows.

(a)

(b)

(c)

(d)

Figure 5: AFM images of the spin-coated mCP: Nd(TTA)₃phen blend films for different doping concentrations: (a) 7 wt.%, (b) 13 wt.%, (c) 16 wt.% and (d) 20 wt.%. The root-mean-square (RMS) roughness values for a, b, c and d are 0.57, 0.54, 0.45 and 0.34 nm, respectively.

Figure 6: EL spectra of mCP (in the visible region) and Nd(TTA)₃phen (7 wt.%) (in the NIR region) at different driving voltages in device A.

Figure 7: EL spectra of mCP (in the visible region) and Nd(TTA)₃phen (13 wt.%) (in the NIR region) at different driving voltages in device B.

Figure 8: EL spectra of mCP (in the visible region) and Nd(TTA)₃phen (16 wt.%) (in the NIR region) at different driving voltages in device C.

Figure 9: EL spectra of mCP (in the visible region) and Nd(TTA)₃phen (20 wt.%) (in the NIR region) at different driving voltages in device D.

Figure 10: (a) Current density versus voltage and (b) EQE versus current density curves measured in the NIR-OLEDs. The linear plots in the inset of Figure 10 (a) are showing a small shift of the J-V curves by increasing the doping concentration.

Table 1. Summary of the singlet and triplet energies of mCP, TTA, and Phen ligands.

Compound	E_{singlet} (eV)	E_{triplet} (eV)	References
mCP	3.56	2.9	[26]
TTA	3.12	2.35	[27]
Phen	3.87	2.09	[27]