

Recent development of near infrared organic light-emitting materials and devices

Jean-Charles Ribierre¹

¹ KOALA Tech Inc.

FiaS 215, 4-1 Kyudai-Shinmachi, Nishi-ku, Fukuoka 819-0388

Phone: +81-92-807-6036 E-mail: ribierre@koala.co.jp

Abstract

Near infrared (NIR) organic light-emitting devices are of interest for a variety of applications including information-secured displays, photodynamic therapy and optical telecommunication. While thermally activated delayed fluorescent (TADF) emitters have been successfully used in high-performance organic light-emitting diodes (OLEDs) operating in the visible spectral range, efficient NIR TADF materials have been rarely reported. Here, we will discuss about the recent development of solution-processable boron difluoride curcuminoid derivatives for high efficiency NIR TADF OLEDs and low threshold organic semiconductor lasers. The results not only provide evidence that the TADF technology is suitable for high performance NIR OLEDs but also open up fascinating opportunities in the context of NIR organic semiconductor lasers.

1. Introduction

There has been a growing interest for the design and the development of novel organic materials and devices that emit light efficiently at wavelengths longer than 700 nm. The current intense research efforts to demonstrate high performance near infrared (NIR) OLEDs and organic semiconductor lasers have been stimulated by their potential applications in important areas such as the telecommunication, defense and biomedical sectors. In fact, the performances of NIR OLEDs have markedly improved when using phosphorescent heavy-metal complexes. Recently, as an alternative, purely organic thermally-activated delayed fluorescent (TADF) emitters^{1,2} have been identified as the third generation of OLED materials and can be used in electroluminescent (EL) devices that harvest both singlet and triplet excitons via efficient reverse intersystem crossing (RISC). Although NIR TADF OLEDs are particularly attractive for a battery of applications, their performances still remain lower and need to be substantially improved via the development of novel high-efficiency TADF emitters.³ The design of NIR TADF emitters with high photoluminescence quantum yield (PLQY) still represents a challenge for several reasons. Firstly, the PLQY generally tends to decrease when the emission is shifted toward longer wavelength due to the competition between the larger non-radiative decay rates and the radiative fluorescence decay rate, in accordance with the energy gap law. Another issue is that stronger aggregation-caused fluorescence quenching often takes place in NIR light-emitting organic thin films.

Here, I will discuss about recent progress in the development of donor-acceptor-donor borondifluoride curcuminoid derivatives as a versatile and simple platform for the molecular engineering of high-efficiency NIR emitters combining thermally-activated delayed fluorescence (TADF) with excellent electroluminescence properties and amplified spontaneous emission (ASE) activity (see Fig. 1) in the NIR spectral region.⁴ Those results suggest that this class of materials is promising for the future realization of electrically-pumped NIR organic semiconductor laser diodes. In the last part of this presentation, I will give a brief introduction about KOALA Tech, a venture startup company from Kyushu University aiming at bringing the new organic semiconductor laser technology to the market.

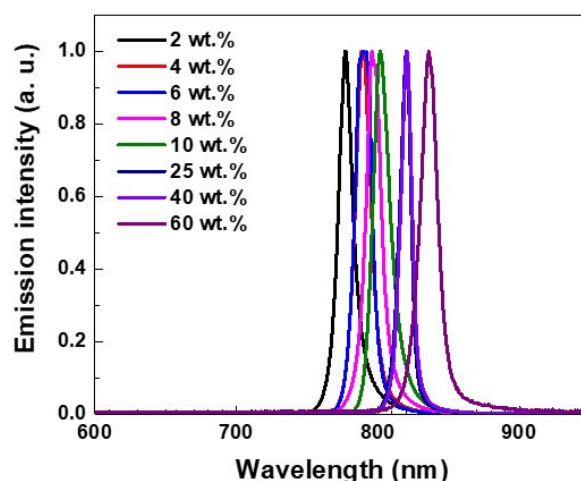


Fig. 1 NIR ASE spectra of organic semiconducting thin films using a borondifluoride curcuminoid derivative as laser dye doping a host material at different doping concentrations ranging from 2 to 60 wt.%.

2. Results

In the first part of this talk, I will report on the realization of NIR TADF OLEDs with a maximum electroluminescence external quantum efficiency (EQE) approaching 10%. The electroluminescent devices used a solution-processable heavy-metal-free donor-acceptor-donor borondifluoride curcuminoid derivative as NIR emitter.^{5,6} This compound shows a rather high photoluminescence quantum yield (up to 65%) in solid matrices with an emission maximum wavelength typically in the range between 700 and 750 nm. Time-resolved

photophysical measurements show that the TADF mechanism of this NIR emitter is due to a reverse inter-system crossing from triplet charge transfer (CT) to singlet CT excited states. In addition, the TADF efficiency is found to strongly depend on the dye concentration in the emissive layer due to the CT character of the excited states and the large dipole moments of this compound.

In the second part of this contribution, I will discuss about the amplified spontaneous emission properties^{7,8} of curcuminoid derivatives in the NIR spectral region. For this purpose, the organic thin films were prepared onto fused silica substrates and photo-excited by a nitrogen laser (excitation wavelength of 337 nm, repetition rate of 8 Hz and pulse width of 800 ps). An optical fiber connected to a charge-coupled device spectrometer was used to measure the emission spectra from the edge of the organic layers. The ASE peak wavelength of those films can be tuned in the NIR by controlling the doping concentration of the emitters. By optimizing the doping concentration of the emitter in the blend, the ASE threshold could be decreased to about 7 $\mu\text{J}/\text{cm}^2$. Although the measured ASE thresholds are higher than the lowest values reported for organic thin films emitting in the visible (which are around 0.1-0.4 $\mu\text{J}/\text{cm}^2$), the obtained values suggest the possibility to realize efficient and tunable NIR organic semiconductor lasers. To validate this statement, optically-pumped NIR organic semiconductor distributed feedback (DFB) lasers are fabricated and showed state-of-the-art performances in terms of low lasing threshold. Overall, this work represents an important step toward the realization of high-efficiency OLEDs and low-threshold organic semiconductor lasers operating in the NIR region. This study provides scopes for the realization of NIR electrically-pumped organic semiconductor lasers.⁹

In the last part of this talk, I will introduce KOALA Tech Inc., an innovative high-tech startup company aiming at accelerating the R&D and overcoming the final obstacles remaining for the use of organic semiconductor laser diodes in commercial products.

3. Conclusions

In conclusions, NIR TADF OLEDs with a maximum external quantum efficiency approaching 10% are demonstrated using donor-acceptor-donor borondifluoride curcuminoid derivatives. Their electroluminescent properties exceed those typically obtained with conventional NIR fluorescent emitters. In addition, curcuminoid derivatives in blend films exhibit low threshold NIR ASE activity, suggesting the possibility to harvest triplet excitons for stimulated emission. This study is particularly relevant for the future development of near infrared organic semiconductor laser diodes.

References

- [1] H. Uoyama et al., *Nature* **492** (2012) 234.
- [2] H. Kaji et al., *Nature Comm.* **6** (2015) 8476.
- [3] A. Zampetti et al., *Adv. Funct. Mater.* **29** (2019) 1807623

- [4] D. H. Kim et al., *Nature Photon.* **12** (2018) 98.
- [5] E. Kim et al., *Org. Biomol. Chem.* **14** (2016) 1311.
- [6] S. Chambon, *Chem. Comm.* **49** (2013) 3555.
- [7] I. D. W. Samuel et al., *Chem. Rev.* **107** (2007) 1272.
- [8] A. J. C. Kuehne et al., *Chem. Rev.* **116** (2016) 12823.
- [9] A. S. D. Sandanayaka et al., *Appl. Phys. Expr.* **12** (2019) 061010.