1. PHD PROJECT DESCRIPTION (4000 characters max., including the aims and work plan, all in English)

Project title: Synthesis and characterization of thermally activated delayed fluorescence emitters and their application in printed electronics.

1.1. Project goals

The aim of the project is the synthesis of new organic compounds exhibiting thermally activated delayed fluorescence (TADF) of good solubility in toluene and insoluble in isopropanol for ink-jet printing. The emitters will be spectrally characterized and prototype OLED panels will be printed. The goal will be achieved by:

- Design of the new organic TADF compounds and prediction their spectral properties based on DFT calculations.
- Synthesis of novel, non-published TADF organic emitters of acceptor-donor structure with 3-alkyl and 3,6-dialkyl carbazole derivatives as a donor moiety, obtained via palladium-catalyzed Kumada-type coupling.
- Characterization of the synthesized TADF compounds i.e. spectral and stability characteristics, CV and other methods.
- Preparation of the prototype OLED diodes using synthesized compounds.

1.2. Outline

Thermally activated delayed fluorescence (TADF) is one of the way in which an electrically excited molecular species can emit electromagnetic radiation. In general, materials that exhibit fluorescence emit light by a fast radiative transition from a singlet excited state to a singlet ground state. The approximate time scale of this phenomenon is in the range of nanoseconds. Some of the materials also give additional light emission within microseconds and this emission is called delayed fluorescence. The process of emission is delayed because of the conversion of excitons from a triplet to singlet state. The TADF process is a type of the E-type delayed fluorescence, where triplet excitons are converted into singlet excitons by reverse intersystem crossing. This phenomenon is thermally activated, but also a small singlet-triplet energy gap (ΔE_{ST}) makes it possible to occur. When it comes to the theory, it is claimed that the internal quantum efficiency of the TADF process is equal to 100%, because all of the triplet excitons can be transformed into singlet excitons. The TADF phenomenon occurs in specific types of molecules. The structure of most commonly used donor-acceptor type TADF emitters involves the presence of electron donating moieties like aromatic amines (i.e. carbazole, phenoxazine) and their derivatives, but also there must be electron accepting groups i.e. phenyl rings with nitrile or trifluoroacetic group. The key factor of the TADF process is to obtain the smallest possible energy gap between first singlet and first triplet excited states of the molecule and maintain high oscillator strength. Small ΔE_{ST} enables the conversion of the triplet states into singlet states with the minimum energy expenditure (like thermal energy) and high oscillator strength ensures that the exciton decay occurs radially.

Molecules that exhibit the TADF properties are of high interest mainly in the electronic industry. Their main application is the Organic Light-Emitting Devices (OLED) technology. Current devices are based on compounds that emit phosphorescence, but their main disadvantage is their composition, durability and stability. Such compounds are complex structures based on rare heavy metals. Rather weak coordination bonds are responsible for the degradation of phosphorescent emitters. In contrast to those compounds, TADF emitters are purely organic compounds of strong covalent bonds. As a result of this feature, TADF compounds are cheaper, greener and have longer lifetime. As another advantages of TADF compounds one can point out lower power consumption, lightweight and higher contrast comparing to traditional LED or LCD devices. Those features, but also the variety of colors and high brightness of such molecules makes them suitable for electronic devices used in displays of smartphones and TV screens, but also as a component of smart OLED packaging. The new idea of smart packaging involves so called ink-jet printing. The whole light emitting device is printed in the label or packaging of the product and enables it to emit light. Such device is thin (i.e. 0.5 mm), can be activated with touch, humidity change, movement or even a smartphone, and it is self-powered because of printed battery. Smart packaging or smart labels are for sure the future. Not only they make the product more interesting, surprising or beautiful, but also can show the customer, for example, how much product is left. It is also possible to make a packaging a kind of display for the customer – with all the information needed. The same approach can be used in advertisement (newspapers).

The main goal of this project is to synthesize novel organic TADF emitters suitable for printing. Proposed structures of those compounds are based on unknown 3-alkyl and 3,6-dialkyl carbazole derivatives as the electron donating part and known acceptor moieties. Proposed structures of donors are shown in figure 1.

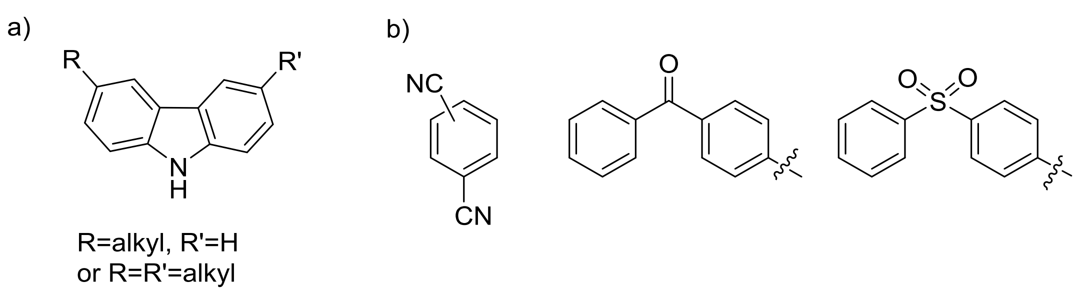

Figure 1. Structures of proposed donors and known acceptors

The alkyl groups are respectively C2 to C10 (i.e. ethyl, propyl, isopropyl etc.). Compounds with methyl and *tert*-butyl groups are known, but the rest are novel and non-published.

Such compounds can be obtained in several ways. The applicant proposes the synthesis of well soluble donor parts via palladium-catalyzed coupling reaction, developed in our team, which approach looks to be the most convenient.

As a first step, the DFT quantum chemical calculations in Gaussian will be carried out to predict the TADF properties of the proposed compounds. Such calculations will provide the information about HOMO/LUMO energy levels, excited state triplet energy and ΔE_{ST}, emission maximum and oscillator strength. Compounds of the best theoretical properties will be directed to synthesis and purification and their purity will be confirmed by GC, and HPLC. The products will be characterized by NMR, UV-Vis, IR, fluorescence measurements and cyclic voltammetry (HOMO/LUMO energy). The PL emission spectra in aerated and degassed solutions (to confirm the TADF effect), at different temperatures (77 K, 200 K, and 300 K), luminescence lifetimes, quantum yields, photostability, and melting point measurements will also be performed. The last part will be selection of charge-transporting layers, stack projecting, preparing ink and printing the prototype OLED diodes.

1.3. Work plan

<u>Year I, semester I:</u>

- Design of the new organic TADF compounds with the use of DFT calculations and prediction of their properties.
- Synthesis and purification of donor parts of designed TADF compounds with the use of developed in our team palladium catalyzed coupling reaction for alkyl carbazoles.

<u>Year I, semester II</u>

- Synthesis and purification of designed TADF compounds containing proprietary alkyl carbazoles.
- Characteristic of the novel TADF compounds – NMR spectra, UV-Vis, IR, GC, HPLC, fluorescence measurements etc.

<u>Year II, semester I</u>

- Synthesis and purification of designed TADF compounds containing proprietary alkyl carbazoles.
- Characteristic of the novel TADF compounds – NMR spectra, UV-Vis, IR, GC, HPLC, fluorescence measurements etc.
- Confirmation of the TADF effect of resulted compounds via PL emission spectra measurements.

<u>Year II, semester II</u>

- Further synthesis, purification and characteristic of the TADF compounds.
- Confirmation of the TADF effect of resulted compounds via PL emission spectra measurements.

<u>Year III, semester I</u>

- Further synthesis, purification and characteristic of the TADF compounds.
- Confirmation of the TADF effect of resulted compounds via PL emission spectra measurements.
- Pre-selection of synthesized compounds, preparing ink for printing and test prints.
- An attempt to construct a prototype OLED diode.

<u>Year III, semester II</u>

- Construction of the prototype OLED diode.
- Synthetic tuning of proprietary emitters (if needed).

- Further synthesis of proprietary TADF emitters and TADF effect confirmation via PL emission spectra measurements.

Year IV, semester I

- Final tuning of emitters (if needed).
- Construction of the prototype OLED diodes.
- Preparation for the doctoral dissertation.

Year IV, semester II

- Final corrections and measurements (if needed).
- Preparation for the doctoral dissertation.

During the studies it is also plan to publish the achieved results and to take part in national and international conferences.

1.4. Literature

1. Zhang, Q.; Li, J.; Shizu, K.; Huang, S.; Hirata, S.; Miyazaki, H.; Adachi, C. 2012, J. Am. Chem. Soc. 134, 14706-14709
2. Yirang Im, Mounggon Kim, Yong Joo Cho, Jeong-A Seo, Kyoung Soo Yook, Jun Yeob Lee, 2017, Chem. Mater. 29, 1946−1963

1.5. Required initial knowledge and skills of the PhD candidate

- Good knowledge of organic chemistry, especially heterocyclic synthesis.
- Practical skills enabling to work in an organic chemistry laboratory.
- Knowledge of Gaussian program and DFT calculations.
- Knowledge of techniques that will be used in the project: IR, NMR, UV-Vis, chromatography techniques etc.
- General predisposition for scientific work – motivation, regularity, willingness to achieve the goal.

1.6. Expected development of the PhD candidate’s knowledge and skills

- Broaden the knowledge on TADF compounds in general, but also on the methods of their synthesis.
- Improve the skills in organic syntheses.
- Acquiring proficiency in using various methods of compound characterization.
- Increase in management of stressful and complicated situations.