UNIVERSITY OF PARDUBICE
FACULTY OF CHEMICAL TECHNOLOGY
Institute of Organic Chemistry and Technology

Michaela Fecková

Organic and organometallic heterocyclic luminescent materials: towards OLED applications

Theses of the Doctoral Dissertation

Pardubice 2021

Study program: **Organic Chemistry**
Study field: **Organic Chemistry**

Author: **Ing. Michaela Fecková**
Supervisors: **prof. Ing. Filip Bureš, Ph.D.** and **assoc. prof. Sylvain Achelle, Ph.D.**
Year of the defence: 2021

References

FECKOVÁ, Michaela. *Organic and organometallic heterocyclic luminescent materials: towards OLED applications.* Pardubice, 2021. XXX pages. Dissertation thesis (Ph.D.). University of Pardubice, Faculty of Chemical Technology, Institute of Organic Chemistry and Technology. Supervisors Prof. Ing. Filip Bureš, Ph.D. and Assoc. Prof. Sylvain Achelle, Ph.D.

Abstract

Since 1987, when the first organic light-emitting diode (OLED) was prepared by C. W. Tang and S. V. Slyke (Eastman Kodak company), there has been a great interest in the development of lighting devices based on organic materials. In this disseration, organic and organometallic luminophores bearing pyrimidine heterocycle as electron-withdrawing moiety are discussed. Three series with different structural features were prepared: (i) 2,4-di(arylvinyl)- and 2,4,6 tri(arylvinyl)pyrimidines with identical or different peripheral electron-donating groups, (ii) 4-arylvinyl- a 4,6-di(arylvinyl)pyrimidines with twisted phenylacridan structure in position 2 of pyrimidine ring and (iii) 2 phenylpyrimidine cyclometalated platinum (II) complexes. Photoluminescence properties of all final derivatives were measured. Structure-photoluminescence relationships within each series were drawn from these results and thoroughly discussed. Interesting luminescence phenomena, such as tuneable emission by protonation, aggregation-induced emission, dual emission, solid-state emission or white light emission, were observed for certain derivatives across the series.

Keywords

organic light-emitting diode (OLED), push-pull chromophore, pyrimidine, platinum, luminescence

Abstrakt

Od roku 1987, kdy byla C. W. Tangem a S. V. Slykem (ve společnosti Eastman Kodak) vyrobena první organická světlo emitující dioda (OLED), zájem o vývoj nových světlo emitujících zařízeních s organickými materiály neustále vzrůstá. V disertační předložené práci jsou diskutovány organické a organokovové luminofory nesoucí pyrimidinový heterocyklus jako elektronakceptorní jednotku. Byly připraveny tři série derivátů s odlišnými strukturními vlastnostmi a to (i) 2,4-di(arylvinyl)- a 2,4,6-tri(arylvinyl)pyrimidiny se stejnými či různými okrajovými elektrondonorními skupinami, (ii) 4-arylvinyl- a 4,6-di(arylvinyl)pyrimidiny s fenylakridinovou vytočenou strukturou v poloze 2 pyrimidinového jádra a (iii) platinové komplexy nesoucí 2-fenylpyrimidinové cyklometalující ligandy. Byly měřeny fotoluminiscenční vlastnosti všech cílových derivátů a z nich vyvozeny základní vztahy struktura-fotoluminiscenční vlastnosti, které byly důkladně diskutovány. Bylo pozorováno několik zajímavých luminiscentních úkazů, jako protonací modulovatelná emise, agregací vyvolaná emise, dvojitá emise, emise v pevném stavu nebo emise bílého světla, pro některé deriváty napříč všemi sériemi látek.

Klíčová slova

organické světlo emitující diody (OLED), push-pull chromofor, pyrimidin, platina, luminescence

Résumé

Depuis 1987, date à laquelle la première diode électroluminescente organique (OLED) a été préparée par C. W. Tang et S. V. Slyke (Eastman Kodak company), il y a eu un grand intérêt pour le développement de dispositifs d'éclairage à base de matériaux organiques. Dans ce manuscrit, des luminophores organiques et organométalliques portant un hétérocycle pyrimidine en tant que groupement attracteur d'électrons sont discutés. Trois séries avec des caractéristiques structurelles différentes ont été préparées: (i) Une série de 2,4-di (arylvinyl)- et de 2,4,6-tri(arylvinyl)pyrimidines avec des groupes électro-donneurs périphériques identiques ou différents, (ii) Une série de 4-arylvinyl- et de 4,6-di(arylvinyl)pyrimidines portant un groupement phénylacridine torsadé en position 2 du cycle pyrimidine (iii) Des complexes de platine (II) cyclométalé à base de 2-phénylpyrimidine. Les propriétés de photoluminescence de tous les dérivés finaux ont été mesurées. Des relations structure-photoluminescence au sein de chaque série ont été tirées de ces résultats et discutées en détail. Des phénomènes de luminescence intéressants, tels que l'émission accordable par protonation, l'émission induite par l'agrégation, l’émission duale, l'émission à l'état solide ou l'émission de lumière blanche, ont été observés pour certains de ces dérivés.

Mots clés

diode électroluminescente organique (OLED), chromophore push-pull, pyrimidine, platine, luminescence

Table of Contents

1. Introduction

In the 1990s, especially in their late years, research of organic electronics started to growth exponentially.[1] Organic semiconductors, curtail part of organic electronics, were developed as an alternative to well-established silicon or gallium arsenide or metal-based inorganic semiconductors.[2] Mechanical properties such as high flexibility and toughness, fabrication at low temperature, in large areas and at low cost are among the main advantages of organic electronics.[3] These advantages and the fact that properties of organic material are easily tuneable by structural modifications largely contribute to the growth of organic electronics research and industry.

Examples of organic electronics are organic light-emitting diodes, which utilize luminescent organic or organometallic semiconductors to convert electrical power into the light.[4] Within a few decades, this technology has transformed from very simple single device, through small displays, into the extravagant light sources and large displays, which currently occupy a position among popular products in marketplace.[5–7] Even though these devices already reach a point of commercialisation, consumers' desire for better performance is a driving force for development of novel and improved materials.

In the OLED device, the light emission process after excitation by external electrical potential is called electroluminescence.[8,9] The first observation of EL phenomenon was done by H. J. Round (personal assistant of G. Marconi) in 1907 on silicon carbide.[10] Between 1950 and 1955, after almost fifty years, A. Bemanose and co-workers at the University of Nancy, France, applied a high alternating voltage on acridine orange spread over cellophane or cellulose surface and reported the first EL originating from organic material.[11] In 1987, C. W. Tang and S. Van Slyke at Eastman Kodak published a paper about first convenient OLED device with 8 hydroxyquinoline aluminium (Alq_3) 25 and diamine 26 layers (*Figure 1*).[12] Ten years after, Pioneer Corporation introduced on market the first commercial OLED for car audio screens. Since that time, a variety of OLED-based products, such as light for general-lighting application, smart watches, cell phones, and even large television displays, have conquered the world market.[6]

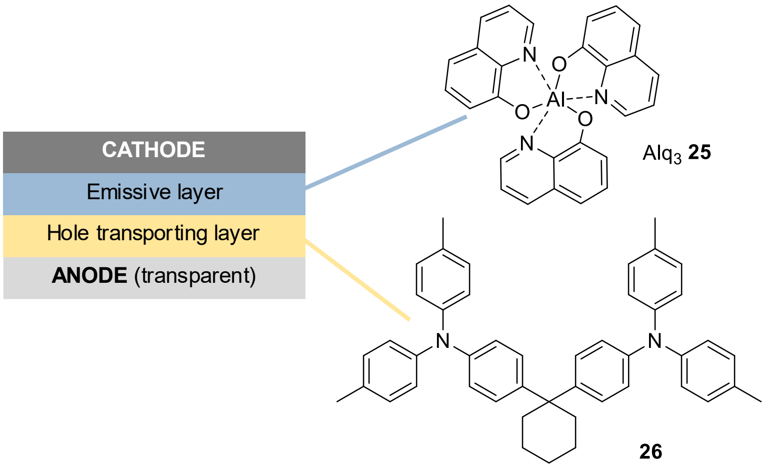


Figure 1. Composition and structure of the very first OLED device by Tang and Van Slyke.[65]

Structure of OLED devices

In OLEDs, stacked layers of different semiconducting materials are placed between two electrodes. Application of electrical potential on electrodes causes movement of electrons from the cathode and holes from the anode through the layers into the emitting layer where both recombine to form exciton. The general structure of multilayer OLED is displayed in *Figure 2*. It consists of anode, following by hole-injection layer (HIL), hole-transport layer (HTL), electron-blocking layer (EBL), emitting layer (EML), hole-blocking layer (HBL), electron-transport layer (ETL), electron-injection layer (EIL) and ends with cathode. A real OLED device does not have to include all aforementioned layers but special requirements, such as good thermal stability, high conductivity, low power-on voltage etc., are necessary for the particular organic materials.

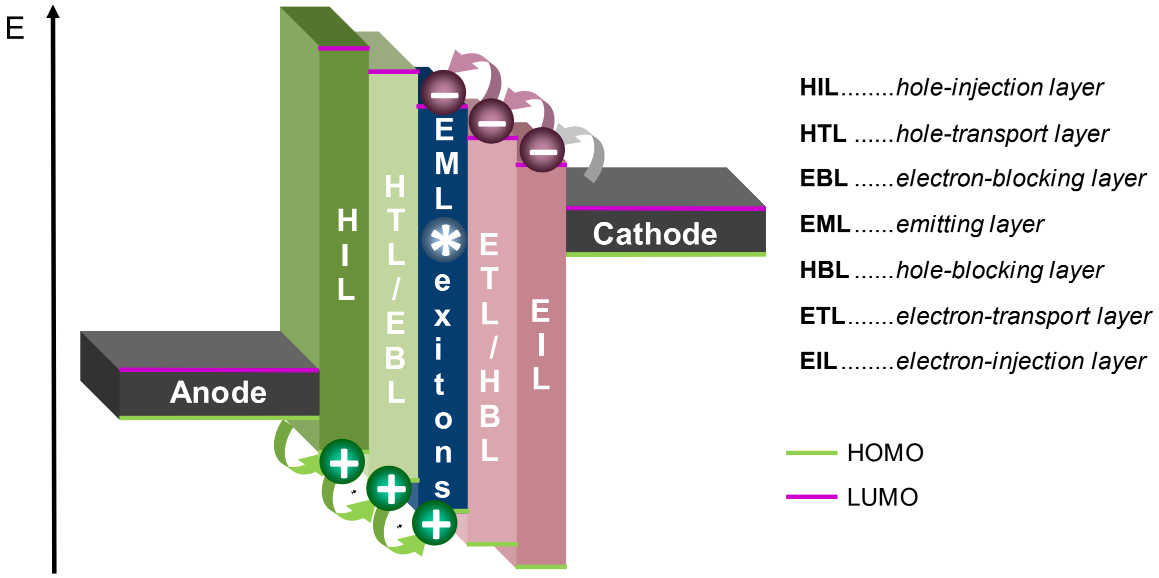


Figure 2. General architecture of an OLED device.

General requests for anode are high transparency, conductivity, good adhesion properties and high work-function to inject hole into the HOMO of organic material.[13] Indium tin oxide (ITO) is the most common choice of anode material. It has good conductivity, high chemical stability, high work function, good transparency (90%) to visible wavelength range and excellent adhesion to substrate. However, indium oxide can migrate into organic layer and devalue emitting properties of OLED. ITO also has high refractive index, which is resulting in 75% loss of the generated photons. Another material for anode is fluorine-doped tin oxide, aluminium-doped zinc oxide and transparent conductive oxides – $Ga_{0.08}In_{1.28}Sn_{0.64}O_3$, $Zn_{0.5}In_{1.5}O_3$ and $Zn_{0.46}In_{0.88}Sn_{0.66}O_3$.[14]

The hole-injection/electron-injection layer helps to reduce energy barrier between the anode/cathode work-function and the HOMO/LUMO level of the emissive layer.[15] Triphenylamine derivatives such as **27** or copper complex of phthalocyanine **28** are widely used as HIL. Selection of EIL can be complicated. Alkali metal halides and metal oxides or lithium quinolate **29** are often employed (*Figure 3*).[14]

The HTL and ETL transport charge carriers into emissive layer.[16] The HOMO level of HTL material should be slightly lower than that of EML for improving charge flow into to the EML with a minimum hole accumulation on their interface. The energy gap should be wide to block transfer of excitons and electrons towards anode. The HTL layer can be doped with electron-accepting p-dopant while conductivity of the ETL can be improved by adding n dopants. The HTL is often used as electron-blocking layer and the ETL as hole-blocking layer. Typical HTL materials are aromatic amines, for example diamino compound **30**, derivative **31** with two carbazole units or spirobifluorene **32**. Lithium quinolate **29**, oxadiazole **33** or phenanthroline **34** are the most-widely used ETL materials (*Figure 3*).[14,17]

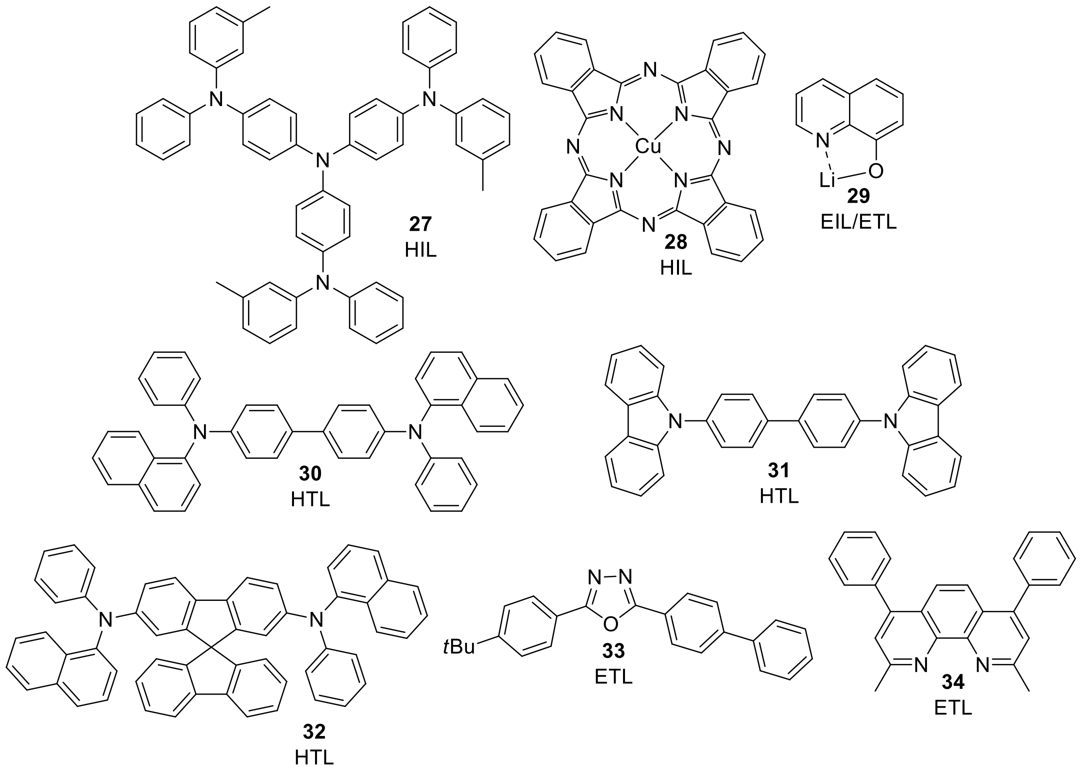


Figure 3. Examples of organic compounds used in OLED devices.

Mg:Ag (10:1), LiF and Mg:Al are favourite materials for cathode. This electrode should have low work-functions and efficient electron injection properties.[17]

Emissive layer in OLED is mostly composed of dopants and host. Dopants are emissive organic semiconductors; these can be generally divided into three categories: (i) small molecules, (ii) conjugated dendrimers and (iii) conjugated polymers. Host materials transport charge carriers, allow excitons formation and simplify radiative recombination. Requirements for the EML materials are high efficiency, lifetime and colour purity. The colour of the generated light depends on the choice of emissive dopant.[18]

Working principle of OLED

Organic material, as a semiconductor, shows high resistance at low electric field.[17] That creates high energy barrier at the interface of an electrode and organic layer. In order to cross this barrier, energy of injected charge carrier must overcome the potential energy barrier. This injection mechanism is called Schottky or thermionic emission. Carriers can also penetrate through the energy barrier, if it is thin enough, in the meaning of tunnel or field emission. A successful hole and electron injection through both processes (*Figure 4*) requires low energy of the barrier and high HOMO and low LUMO levels of the organic material.

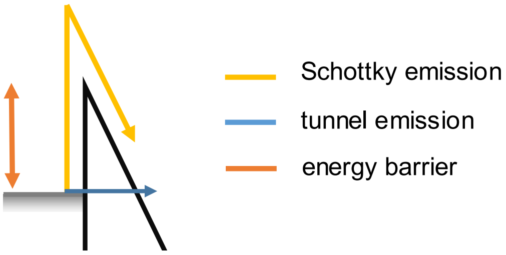


Figure 4. Schottky and tunnel emission.

The thin layer in OLED are in the most cases composed of amorphous organic material, therefore the charge transfer cannot be explained by the band-like transfer as in crystalline semiconductors. Thus, the hoping transport mechanism has been proposed to explain charge movement through the organic layers. In this scenario, charge is transferred by successive jumping from one molecule to the neighbour molecule. However, charge transfer in this manner is low 10^{-7}–10^{-2} $cm^2.V^{-1}.s^{-1}$).

When holes and electrons reach the emissive layer, they recombine in exciton.[15,17,19,20] It usually occurs as two-step process. Firstly, loosely bonded triplet or singlet polaron pairs (charge-transfer excitons) are formed. Subsequently, they turn into neutral singlet or triplet forms. In many cases, emissive material suffers from concentration quenching. As a solution, small amount of emitters (guests) can be doped into host matrix. It is a way how to increase EQE and also tune the light colour of emitted light. In this system, energy transfer takes place between the host (exciton donor) and the guest (exciton acceptor) by Förster or Dexter mechanism. Förster is long range dipole-dipole mechanism between singlet states typical for fluorescent emitters. On the other hand, Dexter one involves short range intramolecular electron exchange between triplets or singlets.

Types of OLEDs

There are many ways to categorize OLED devices. For the main purposes of this work, sorting OLEDs into three generations according to their emissive layer seems to be the most suitable way. This sorting is based on a mechanism of harvesting excitons by the emitting media, see Figure 22. Charge recombination in emissive layer corresponds to spin statistics in 25% of singlet and 75% triplet excitons.[86] The first-generation OLED is fabricated with purely organic fluorescent emitter, and therefore, can use only singlet excitons and achieve only 25% of internal quantum efficiency (IQE). The second-generation OLEDs utilize phosphorescent emitters with heavy metals, which can harvest triplet excitons and also remaining 25% of singlets by intersystem crossing. Third-generation OLEDs possesses so called thermally-activated delayed fluorescent (TADF) material in their emissive layer, which can be organic and also organometallic compound.[87] These materials are able to reach both singlets and triplets by reverse intersystem crossing, which is the mechanism converting triplet excitons to singlets by tapping into the thermal energy, without the need to use rare and expensive elements. So, the IQE for the second- and third-generation OLED can theoretically reach up to 100%.[88] A small energy gap between the S and T energy levels is crucial for both transferring mechanisms ISC and RISC.[68] The organic TADF emitters possess combined advantages of the first- and second-generation OLEDs, i.e., high stability and high luminance efficiency and metal-free composition with low-cost fabrication. In addition, these allow producing stable deep-blue light, which had always been problematic for the second-generation OLED devices.

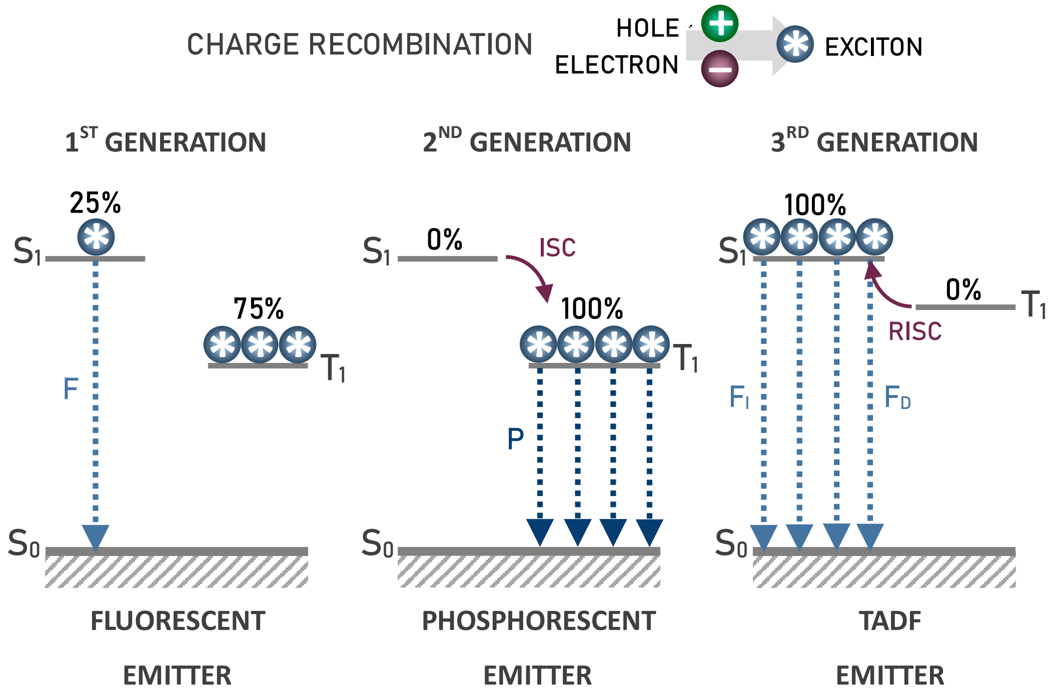


Figure 5. Excitons harvesting mechanism in the 1st, 2nd and 3rd generation OLEDs.

2. Aim of theses

- Create a literature review focused on pyrimidine-based organic and organometallic luminophores and their applications in OLED devices.
- Synthesise novel luminophores with pyrimidine electron-withdrawing group and various electron-donating groups. Verified their as well as all intermediates' structures and purity by standard analytical measurements.
- Conclude structure-luminescence relationships based on experimental and theoretical photophysical data.

3. Result and discussion

3.1. The development of a new series of pyrimidine chromophores based on 2,4-di(arylvinyl)- and 2,4,6-tri(arylvinyl)pyrimidines

Third chapter of doctoral thesis concerned synthesis and photophysical study of 2,4-di(arylvinyl)- and 2,4,6-tri(arylvinyl)pyrimidines, see general structures in *Figure 6*.

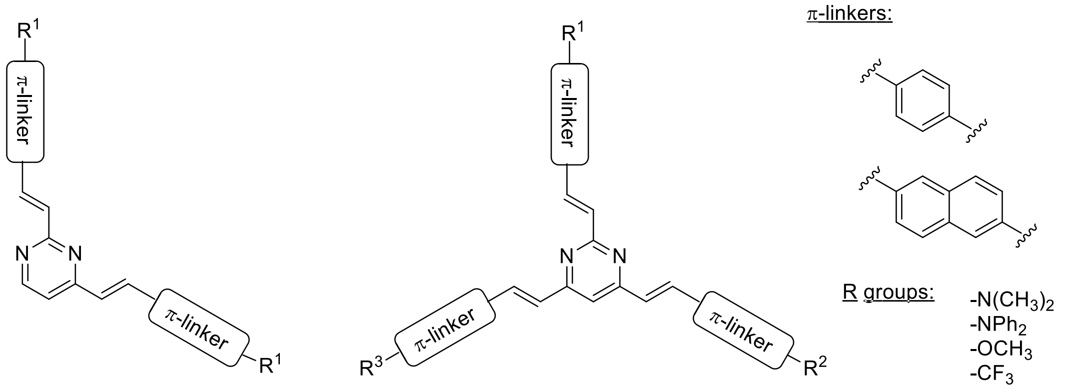
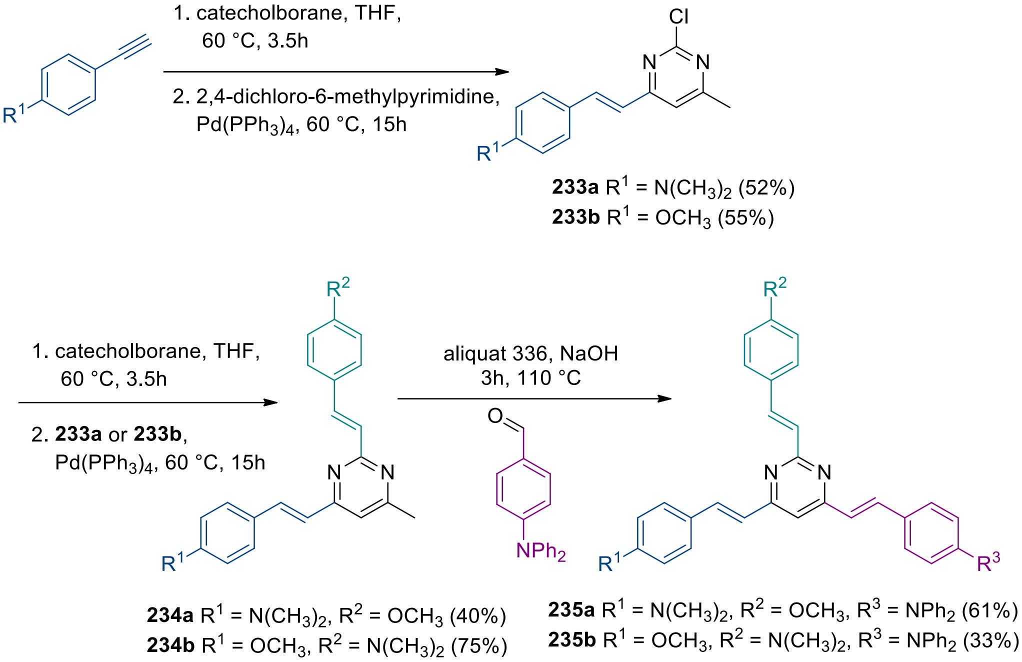


Figure 6. Design of a novel series of 2,4-di(arylvinyl) and 2,4,6-tri(arylvinyl)pyrimidines.

2,4-Distyrylpyrimidines were synthesized from 2-chloro-4-methylpyrimidine in two steps. The first step was a Suzuki-Miyaura coupling in the presence of styrylboronic acid formed *in situ* from the corresponding alkynes. The second step was a Knoevenagel condensation of an aldehyde on the methyl group. Four chromophores of this type were obtained. 2,4,6-Tristyrylpyrimidines were synthesized from 2-chloro-4,6-dimethylpyrimidine or 2,4-dichloro-6-methylpyrimidine in two or three steps respectively. In the first case, the chromophores were obtained by Suzuki coupling followed by double Knoevenagel condensation. The C4 and C6 substituents were then identical. In the second case, a Suzuki monocoupling is carried out regioselectively on the C4 position of the pyrimidine, followed by a second Suzuki coupling on the C2 position of the pyrimidine and finally a Knoevenagel condensation of an aldehyde can be carried out on the. methyl in the C6 position (*Scheme 1*). A total of 21 2,4,6-tristyrylpyrimidines were thus obtained.



233a $R^1 = N(CH_3)_2$ (52%)
233b $R^1 = OCH_3$ (55%)

234a $R^1 = N(CH_3)_2$, $R^2 = OCH_3$ (40%)
234b $R^1 = OCH_3$, $R^2 = N(CH_3)_2$ (75%)

235a $R^1 = N(CH_3)_2$, $R^2 = OCH_3$, $R^3 = NPh_2$ (61%)
235b $R^1 = OCH_3$, $R^2 = N(CH_3)_2$, $R^3 = NPh_2$ (33%)

Scheme 1. Synthesis of 2,4,6-tri(arylvinyl)pyrimidines ***235****.*

Pyrimidine ring does not show three-fold symmetry and this fact brings interesting and uncommon optical properties compared to multi-branched common chromophores with C_3 symmetry. Generally, the photophysical behaviour is given by peripheral substituent(s) attached in C4/C6 positions. However, when the C2 substituent was stronger electron-donating group than substituents in C4/C6 positions, the ICT dominates from the C2 position, and photophysical properties were mainly dependent on the substituent attached on C2 arm. Moderate to high fluorescence quantum yields were observed for most of the final compounds in CH_2Cl_2 solution. The emission solvatochromism of chromophores was studied in various aprotic solvents. While increasing the polarity of the solvent has only limited effect on the position of absorption maxima, the emission bands have been red-shifted, a typical characteristic of chromophores possessing intramolecular charge transfer. The emission spectra of compound **232k** are shown in *Figure 7*. In the case of a polar solvent, the intramolecular charge transfer between the peripheral electro-donor units and the central pyrimidine nucleus increases the dipole-dipole interaction between the chromophore and the solvent molecules, resulting in relaxation of the solvent and a decrease in of the energy of the excited state.

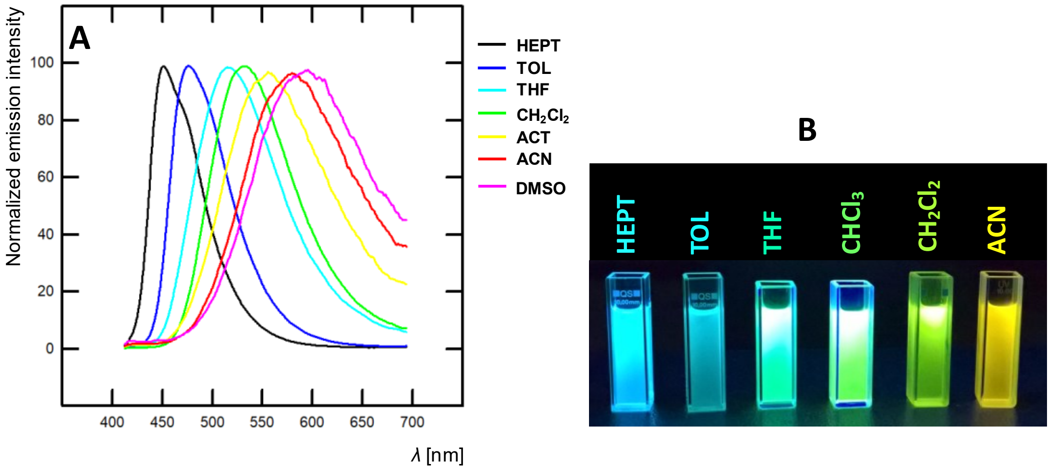


*Figure 7. (A) Normalized emission spectra of **232k** in different solvents. (B) Picture of **232k** colour change in different solvents taken under UV irradiation (hand-held lamp λ = 254 nm).*

Absorption and emission properties were studied during addition of an acid. For amino-substituted derivatives, protonation led to a dramatic quenching of the emission. However, in the case of final derivatives with peripheral methoxy groups, protonation resulted in formation of a new red-shifted emission band. An example of modification of the emission spectrum upon addition of acid is shown in *Figure 8*.

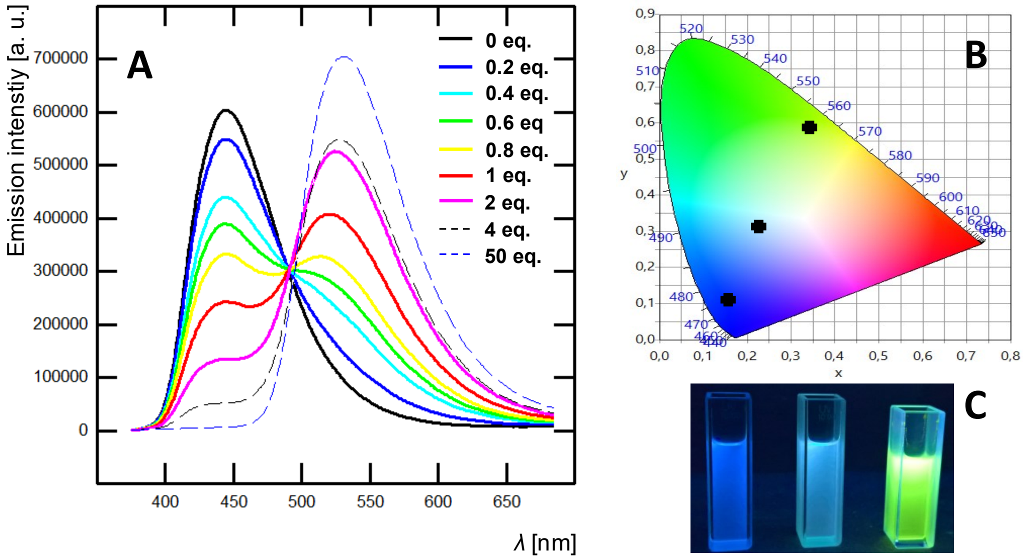


*Figure 8. (A) Emission spectra of chromophore **232q** with progressively increasing amount of acid in CH_2Cl_2 (λ(exc) = 380 nm). (B) 1931 CIE diagram of neutral, partially protonated and fully protonated **232q**. (C) Picture of CH_2Cl_2 solution of neutral (left), equilibrium (middle) and protonated (right) 232q taken un UV irradiation (hand-held lamp λ = 254 nm).*

2PA study of one-, two- and three-branched pyrimidine chromophores with peripheral amino substitution was also performed. Compared to the vast majority of existing tripodal systems, the 2,4,6-tristyrylpyrimidines studied here do not have C_3 symmetry. For this reason, the one- and two-photon absorption spectra of 4,6-distyrylpyrimidines and 2,4,6-tristyrylpyrimidines are similar. Interestingly, while the one-photon absorption spectra of one-branched versus two- or three-branched systems are spectrally shifted, there is almost no spectral shift in the main spectral 2PA band. An improvement in nonlinear responses was observed as the number of branches increased. We have therefore developed here a strategy, which improves two-photon absorption while maintaining the spectral position. More precisely, two-photon absorption cross-section values up to 500 GM in dichloromethane were obtained for the chromophore of structure A–(π-D)$_3$ with three donor groups of the NPh$_2$ type (*Figure 9*).

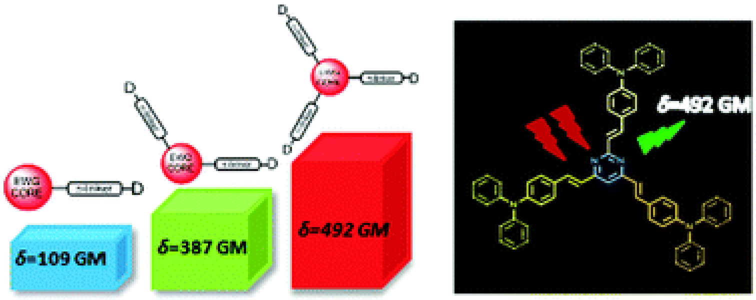


Figure 9. 2PA cross-sections of N, N-diphenylaminostyrylpyrimidines with increasing number of branches.

3.2. 9,9-Dimethylacridan-substituted phenyl(arylvinyl)-pyrimidines as potential emitter for WOLED

A series of six new chromophores with pyrimidine heterocycle as central electron-withdrawing unit was prepared. Acridan moiety was connected to the C2 pyrimidine position via 1,4-phenylene linker and C4(C6) positions were extended by arylvinyl π-conjugated system with peripheral methoxy or diphenylamino donors. (*Figure 10*). The steric hindrance of the acridine group leads to a twisted geometry, as shown by the structures by X-ray diffraction obtained.

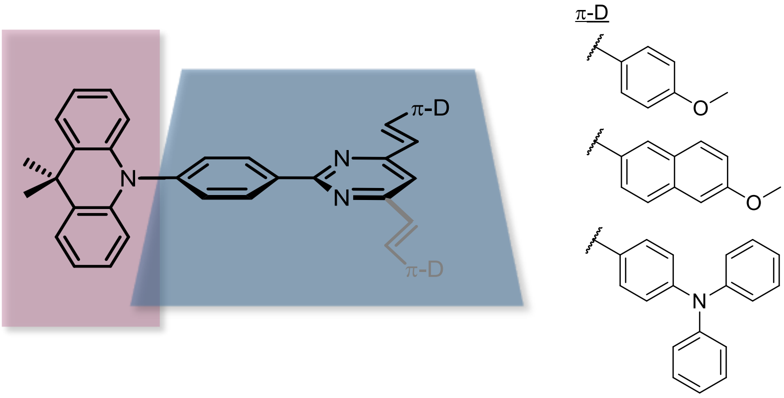
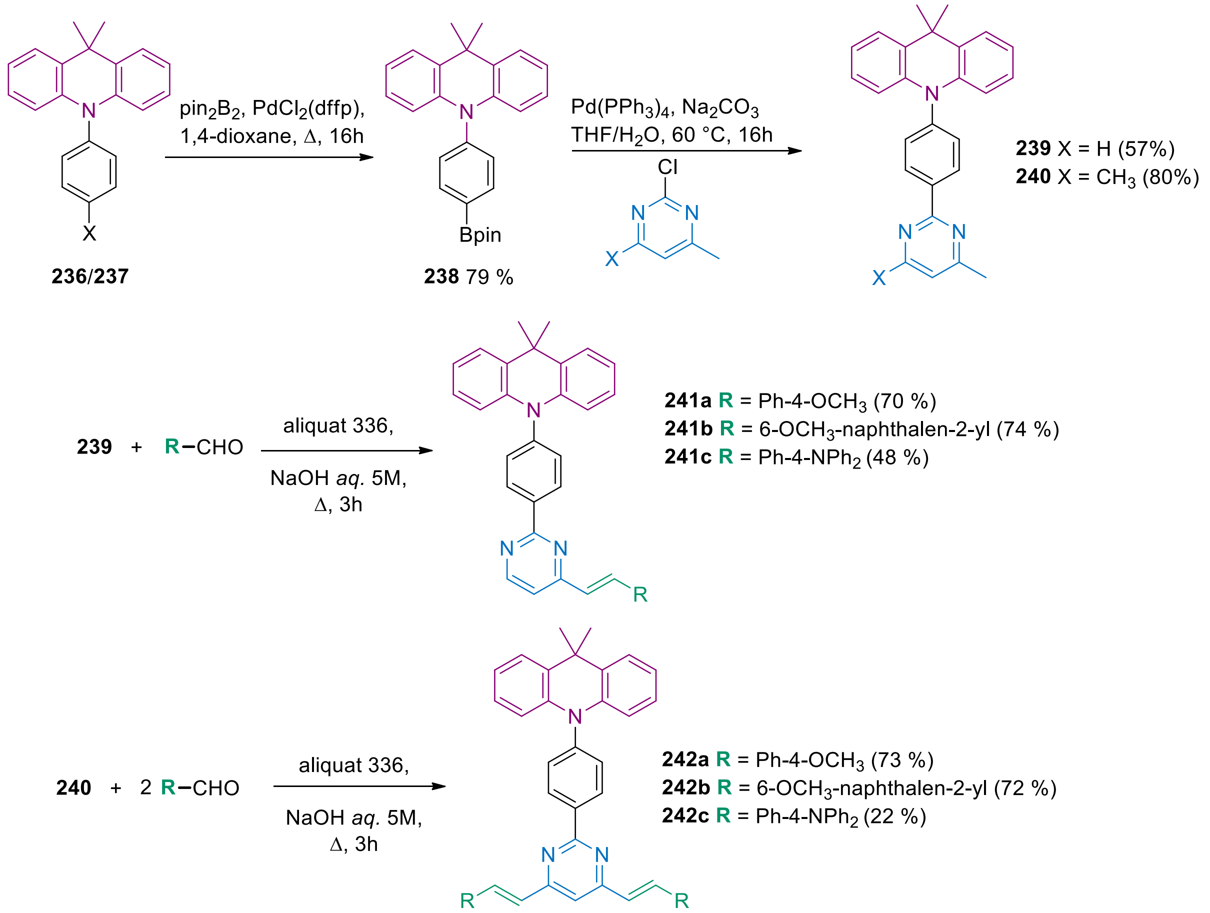


Figure 10. Structures of studied chromophores.

The first synthetic step, an interconnection of the acridine and phenylene unit, revealed to be challenging, however appropriate reaction conditions were found. The remaining synthesis was straightforward. Final derivatives were obtained by Suzuki-Miyaura C-C reaction of 2-chloro-4-methyl or 2-chloro-4,6-dimethylpyrimidine and ester of 4-acridanphenyl boronic acid followed by Knoevenagel reaction between pyrimidine methyl group(s) and corresponding aromatic aldehyde, with satisfying yields (*Scheme 2*).



*Scheme 2. Synthesis of final chromophores **241** and **242**.*

DSC analysis showed that peripheral C4/C6 electron-donating units affected the thermal properties only slightly, while the presence of acridan unit caused high thermal stability with temperatures of decomposition reaching almost 400 °C. The X-ray analysis revealed twisted acridan structure with torsion angles around 85° and also confirmed the *E* configuration of C4(C6) double bonds.

Results of photophysical measurements showed significant differences in photophysical behaviour of methoxy (**a** and **b**) and diphenylamino compounds (**c**). Single-band emission, both in solution and solid-state, high fluorescence quantum yield in CH_2Cl_2 and strong positive emission solvatochromism were observed for diphenylamino derivates (*Figure 11*).

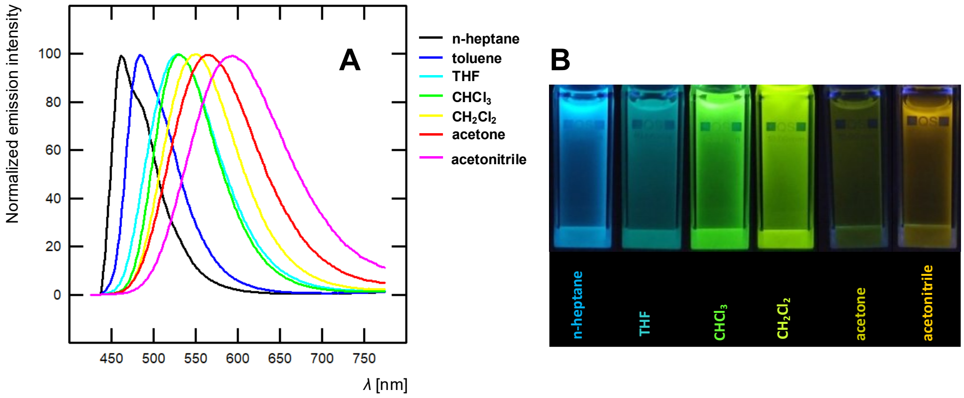


*Figure 11. (A) Emission spectra of **242c** in different aprotic solvents. (B) Pictures of **242c** solutions in different solvents taken under the UV hand lamp (λ = 254 nm).*

Meanwhile, methoxy derivatives exhibited very poor fluorescence in CH_2Cl_2 solution, which enhanced in nonpolar *n*-heptane and further slightly increased after deoxygenation. Methoxy-substituted compounds also exhibited intense AIE and dual emission in THF solution and solid state (*Figure 12*).

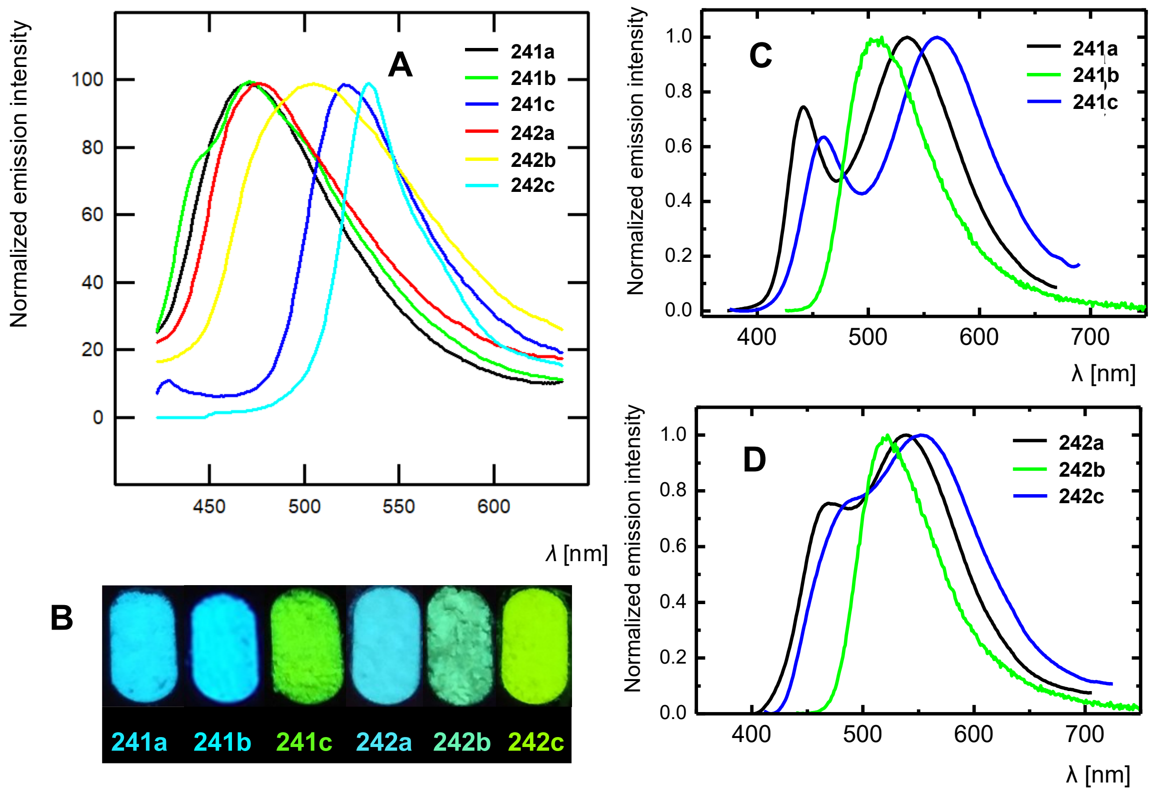
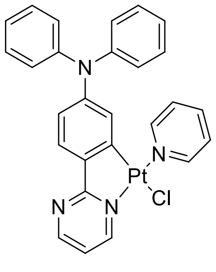


Figure 12. (A) Normalized emission spectra of solid-state chromophores 241 and 242. (B) Picture of powdered final compounds under UV lamp (λ_{em} = 254 nm). Emission spectra of neat film of compounds 241 (C) and 242 (D).

The shorter-wavelength band was attributed to emission from the LE state and the longer-wavelength band was assigned to emission from the ICT/TICT excited state with long lifetime. The colour of the dual emission in thin films was close to white, which makes these compounds potential material for development of single emitter WOLEDs. The anticipated TADF behaviour was not observed, probably due to none oscillator strength of the HOMO → LUMO transition did not possess any oscillator strength, nevertheless unexpected photophysical properties were obtained for methoxy derivatives (**a** and **b**). DFT calculation showed that, despite the HOMO is being localized on the acridan unit, it was completely isolated and did not affect the fundamental absorption properties. These are fully controlled by the peripheral methoxy or diphenylamino electron-donating groups bearing HOMO–1.

3.3 Solid state emitting phenylpyrimidine platinum complexes

The last studied subject was oriented towards organometallic chemistry. Five new platinum(II) complexes bearing phenylpyrimidine cyclometalated ligands with various substituents as well as pyridine and chlorine monodentate ligands were prepared (*Figure 13*).



243

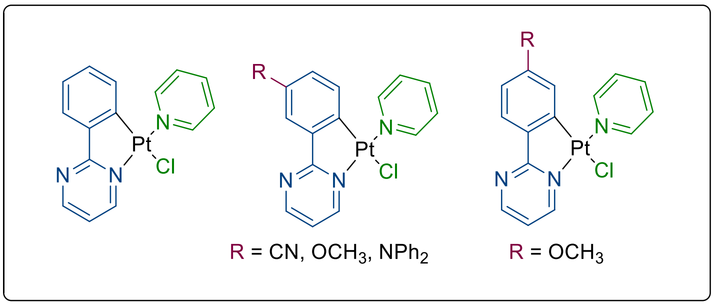


Figure 13. Structures of compound ***243*** *and designed Pt complexes* ***245****.*

All complexes were obtained in moderate to good yields. X-ray analysis and DFT calculations revealed square-planar structure of the central platinum atom and possible rotation of pyridine along Pt-N axis. This rotation caused low or non-existing emission in the solution with a dramatic enhancement in the solid-state, in which the rotation was restricted. As far as the influence of substitution is concerned, presence of electron-donating group in alternating position towards Pt atom resulted in significant increase in the emission quantum yields. The yield in the solution was found up to 0.4 for complex **245c** and excited state lifetimes around 10 μs and red-shift of the emission spectra was recorded in the solid-state (*Figure 14*).

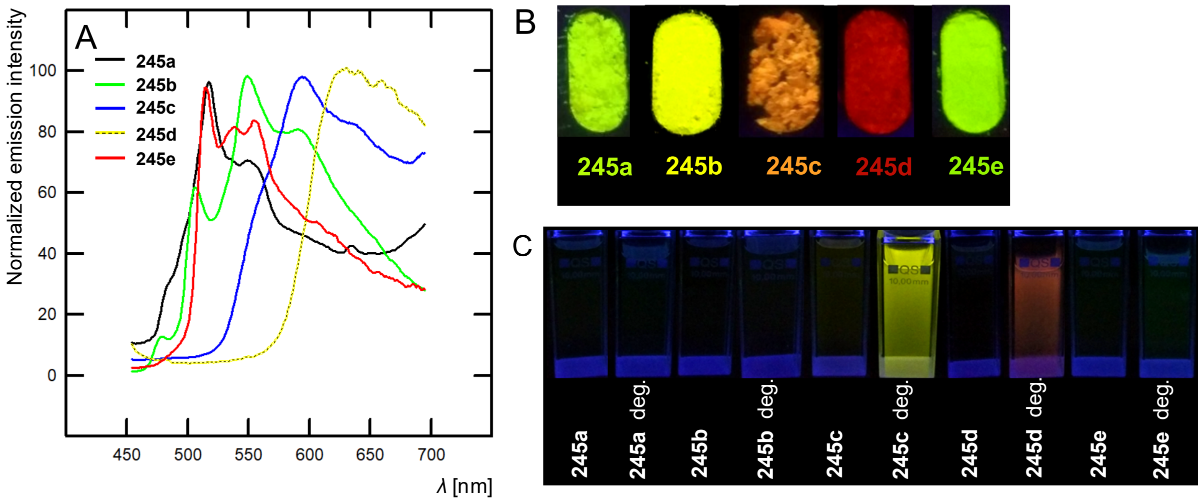


Figure 14. (A) Solid state normalized emission spectra of powdered ***245****. Pictures of (B) powdered and (C) oxygenated and deoxygenated CH_2Cl_2 solutions of* ***245*** *taken under UV-lamp (λ_{em} = 254 nm).*

Strong emission of these complexes in the solid-state makes them promising candidates for their incorporation in OLED devices.

4. Conclusions and perspectives

This dissertation describes results of work concerning pyrimidine-based organic and organometallic luminescent materials suitable for application in OLED technology. The first chapter was dedicated to definition of general concepts and terms, physical quantities and phenomena used for description of luminescence. Basic relationships between structure and luminescence of organic compounds as well as an effect of environment on luminescence were also discussed. Second half of the first chapter contains description of organic semiconductors in the context of OLED technology. The general structure of OLED devices, working principle and ways of OLED's characterisation are also included. In the end, three types of OLED were distinguished based on mechanism how emitters harvest light.

Second chapter began with description of pyrimidine heterocycle and its role in organic materials. Subsequently, fluorescent push-pull chromophores were introduced in context of influence of structural changes on photophysical properties. Short overview of basic synthetic approaches towards building pyrimidine-based chromophores concluded the first part of the second chapter. The main purpose of the second part was to present wide use of pyrimidine containing luminescent materials. Fluorescent probes for detection of solvent polarity, cations, nitrogen explosive and bioimaging were presented. A few examples to achieve white light emission by partial protonation of pyrimidine chromophore were also included. Finally, the end of the second chapter was dedicated to highlight use of pyrimidine organic and organometallic luminophores in OLED devices.

Results of this doctoral work were summarized in three chapters, which were sorted based on the main structural motive, and consequently different photophysical features, of each series. The unified organisation of each chapter starts with the synthesis of target molecules following by results of DSC and X-ray measurements. Subsequent focus was put on photophysical properties of final derivatives and each chapter ended with results of theoretical calculations.

The first series of final derivatives included 2,4-di(arylvinyl)- and 2,4,6-tri(arylvinyl)pyrimidines, from which 23 derivatives were novel structures. Pyrimidine ring was used as a central electron-withdrawing group connected through arylvinylene bridges with mostly electron-donating groups at periphery. Synthesis of these molecules involved Suzuki-Miyaura C-C reaction and Knoevenagel condensation, which allowed preparing derivatives with identical or different substitution on each branch. Vast majority of final molecules exhibited measurable emission and their photophysical properties were mostly affected by electronic nature of C4 and C6 substituents. However, when comparing stronger electron-donor appended in C2 or C4 and C6, both position and intensity of emission spectra were dictated by the C2 substitution. For all emissive derivative, significant positive emission solvatochromism was observed. Modulation of emission colour between dark blue and yellowish green of one final chromophore was achieved by gradual protonation of its solutions. In collaboration with research group of Prof. Mihalis Fakis, University of Patras (Greece), influence of type of acid on absorption, emission and excited state dynamics were studied for diphenylamino-substituted 4,6-distyryl and 2,4,6-tristyrylpyrimidines. In collaboration with Dr. Claudine Katan and Dr. Arnaud Fihey, Université de Rennes 1 as well as Dr. Jean-Pierre Malval and Dr. Arnaud Spangenberg, Université de Haute Alsace (France), influence of branching number of styrylpyrimidines on their photophysical properties was studied. It should be highlighted that the low symmetry given by the pyrimidine ring resulted in increase of 2PA cross-section up to 500 GM within the same spectral region with each additional branch. Concerning the perspectives of multibranched arylvinylpyrimidines, two series of novel derivatives are proposed, see *Figure 15*. Based on the fact, that derivatives with the electron-withdrawing CF3 group in C2 position exhibited the most intense emission and also dual emission during protonation, studying the effect of different electron-withdrawing group in C2 position could potentially lead to interesting results. As a second series styrylpyrimidine-based dendrimers are proposed. The higher number of branches could potentially further increase the 2PA response.

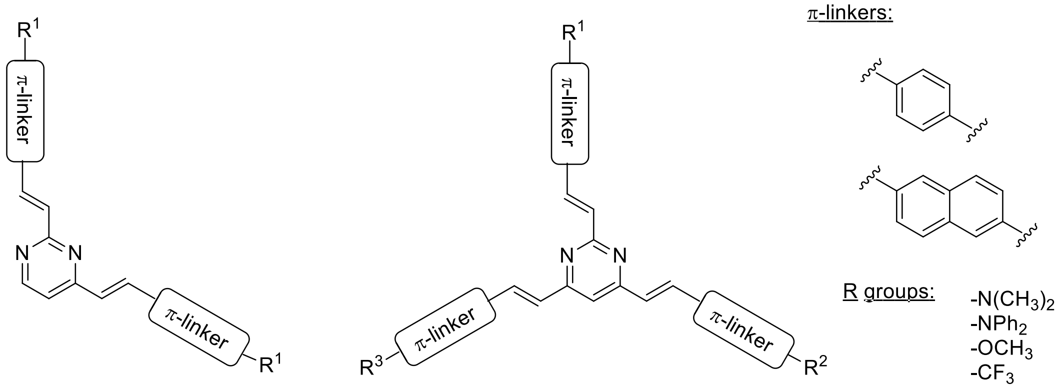


Figure 15. Proposed structures of novel styrylpyrimidines.

Second project concerned 4-arylvinyl- and 4,6-di(arylvinyl)pyrimidines with phenylacridan structure in C2 position of pyrimidine as potential TADF emitters. Six novel chromophores were prepared and fully characterized. The presence of phenylacridan moiety brought a high thermal robustness into these structures. Final derivatives can be divided into two groups with different photophysical properties. Firstly, derivatives with diphenylamino electron-donors in C4/C6 positions exhibited similar properties to those of previously discussed styrylpyrimidines such as high fluorescence quantum yield in moderately polar solvent (CH_2Cl_2), strong positive emission solvatochromism, lower fluorescence quantum yield in low polar solvent (*n*-heptane) and no change in emission intensity after deoxygenation of their solution. On the other hand, derivatives with methoxy group showed significant emission in n heptane solution with increase upon deoxygenation, aggregation-induced emission and dual emission of white light in both thin films and solution (THF or acetone). Although, their anticipated TADF behaviour was not observed, above mention emission phenomena makes them a very promising materials for fabrication of WOLED device based on single emitter.

Last project included synthesis and study of photophysical properties of platinum complexes with ancillary Cl– and pyridine ligand and cyclometaled 2-phenylpyrimidine ligands with substituents both in alternating and non-alternating position towards platinum atom. All complexes showed luminescence in solid-state, however, derivatives with electron-donating groups in alternating position exhibited the most interesting photophysical properties, which makes them promising candidates for utilization as phosphorescent emitters in OLED. Replacement of chlorine atom by different ligands, substitution of the pyrimidine ring and study of their influence on luminescent properties is currently under investigation by Mariia Hruzd, Université de Rennes 1 (France).

List of References

[1] T. W. Kelley, P. F. Baude, C. Gerlach, D. E. Ender, D. Muyres, M. A. Haase, D. E. Vogel, S. D. Theiss, *Chem. Mater.* **2004**, *16*, 4413–4422.

[2] J. M. Shaw, P. F. Seidler, *IBM J. Res. Dev.* **2001**, *45*, 3–9.

[3] M. Reyes-Reyes, D. L. Carroll, W. Blau, R. López-Sandoval, *J. Nanotechnol.* **2011**, *2011*, 589241.

[4] C. H. (Fred) Chen, W.-S. Wen, C.-T. Chen, in *Encyclopedia of Modern Optics*, Elsevier, **2018**, pp. 64–69.

[5] In *OLED Display Fundamentals and Applications*, John Wiley & Sons, Inc., Hoboken, New Jersey, **2017**, pp. 1–5.

[6] N. T. Kalyani, H. Swart, S. J. Dhoble, in *Principles and Applications of Organic Light Emitting Diodes (OLEDs)*, Elsevier, **2017**, pp. 205–225.

[7] G. Zissis, in *LEDs for Lighting Applications* (Ed.: P. Mottier), ISTE, London, UK, **2009**, pp. 1–27.

[8] N. T. Kalyani, H. Swart, S. J. Dhoble, in *Principles and Applications of Organic Light Emitting Diodes (OLEDs)*, Elsevier, **2017**, pp. 1–37.

[9] N. T. Kalyani, H. Swart, S. J. Dhoble, in *Principles and Applications of Organic Light Emitting Diodes (OLEDs)*, Elsevier, **2017**, pp. 39–64.

[10] H. J. Round, *Electr. World* **1907**, *49*, 309.

[11] A. Bemanose, M. Comte, P. Vouaux, *Journal of Chemical Physicsique* **1953**, *50*, 64–69.

[12] C. W. Tang, S. A. VanSlyke, *Appl. Phys. Lett.* **1987**, *51*, 913–915.

[13] In *Organic Light-Emitting Transistors*, John Wiley & Sons, Inc, Hoboken, NJ, **2016**, pp. 5–43.

[14] N. T. Kalyani, H. Swart, S. J. Dhoble, in *Principles and Applications of Organic Light Emitting Diodes (OLEDs)*, Elsevier, **2017**, pp. 141–170.

[15] C. Adachi, S. Lee, T. Nakagawa, K. Shizu, K. Goushi, T. Yasuda, W. J. Potscavage, in *Organic Electronics Materials and Devices* (Ed.: S. Ogawa), Springer Japan, Tokyo, **2015**, pp. 43–73.

[16] U. Wurfel, A. Cuevas, P. Wurfel, *IEEE J. Photovoltaics* **2015**, *5*, 461–469.

[17] D.-G. Moon, in *Encyclopedia of Modern Optics*, Elsevier, **2018**, pp. 232–239.

[18] S. H. Ko, Ed. , *Organic Light Emitting Diode - Material, Process and Devices*, InTech, **2011**.

[19] Z. Dechun, in *Organic Light-Emitting Diodes (OLEDs)*, Elsevier, **2013**, pp. 114–142.

[20] In *OLED Display Fundamentals and Applications*, John Wiley & Sons, Inc., Hoboken, New Jersey, **2017**, pp. 7–59.

List of Student’s Published Works

Publication

[1] FECKOVÁ, Michaela, LE POUL, Pascal, ROBIN-LE GUEN, Françoise, ROISNEL, Thierry, PYTELA, Oldřich, KLIKAR, Milan, BUREŠ, Filip, ACHELLE, Sylvain. 2,4-Distyryl- and 2,4,6-tristyrylpyrimidines: Synthesis and Photophysical Properties, *Journal of Organic Chemistry*, 2018, 83, 11712–11726.

[2] TYDLITÁT, Jiří, FECKOVÁ, Michaela, LE POUL, Pascal, PYTELA, Oldřich, KLIKAR, Milan, RODRÍGUEZ-LÓPEZ, Julián, ROBIN-LE GUEN, Françoise, ACHELLE, Sylvain. Influence of Donor-Substituents on Triphenylamine Chromophores Bearing Pyridine Fragments, *European Journal of Organic Chemistry*, 2019, 9, 1921–1930.

[3] KOURNOUTAS, Fotis, KALIS, Ioannis Konstantinos, FECKOVÁ, Michaela, ACHELLE, Sylvain, FAKIS, Mihalis. The effect of protonation on the excited state dynamics of pyrimidine chromophores, *Journal of Photochemistry & Photobiology A: Chemistry*, 2020, 391, 112398.

[4] KOURNOUTAS, Fotis, FIHEY, Arnaud, MALVAL, Jean-Pierre, SPANGENBERG, Arnaud, FECKOVÁ, Michaela, LE POUL, Pascal, KATAN, Claudine, ROBIN-LE GUEN, Françoise, BUREŠ, Filip, ACHELLE, Sylvain, FAKIS, Mihalis. Branching effect on the linear and nonlinear optical properties of styrylpyrimidines, *Physical Chemistry Chemical Physics*, 2020, 22, 4165–4176.

[5] FECKOVÁ, Michaela, LE POUL, Pascal, BUREŠ, Filip, F. Robin-le Guen, S. Achelle: Nonlinear optical properties of pyrimidine chromophores, *Dyes and Pigments*, 182, 108659. 10.1016/j.dyepig.2020.108659

[6] FECKOVÁ, Michaela, I. K. Kalis, T. Roisnel, LE POUL, Pascal, PYTELA, Oldřich, KLIKAR, Milan, ROBIN-LE GUEN, Françoise, BUREŠ, Filip, FAKIS, Mihalis, ACHELLE, Sylvain. Photophysics of 9,9-Dimethylacridan-Substituted Phenylstyrylpyrimidines Exhibiting Long-Lived Intramolecular Charge-Transfer Fluorescence and Aggregation-Induced Emission Characteristics, *Chemistry – A Eurupean Journal*, 2021, 27, 1145–1159.

[7] FECKOVÁ, Michaela, KAHLAL, Samia, ROISNEL, Thierry, SAILLARD, Jean-Yves, BOIXEL, Julien, HRUZD, Mariia, LE POUL, Pascal, GAUTHIER, Sébastien, ROBIN-LE GUEN, Françoise, BUREŠ, Filip, ACHELLE, Sylvain. Cyclometallated 2-phenylpyrimidine derived platinum complexes: Synthesis and photophysical properties, *European Journal of Inorganic Chemistry*, 10.1002/ejic.202100155 Accepted Article

Oral communications:

[1] S. Achelle, M. Klikar, M. Fecková, F. Robin-le Guen, P. le Poul, F. Bureš: Diazine as building-blocks for the synthesis of nonlinear optical chromophores, Barrande-Vltava French-Czech Chemistry Meeting, Strasbourg (France), 27.-28. 8. 2018, p. 25.

[2] M. Fecková, S. Achelle, F. Robin-le Guen, P. le Poul, F. Bureš: 2,4-Distyryl and 2,4,6-tristyrylpyrimidines: synthesis and optical properties, Journées Scientifiques SCF-BLP, Tregastel (France), 1.–3. 4. 2019, p. 38.

[3] M. Fecková, F. Bureš, S. Achelle, P. le Poul, F. Robin-le Guen: Deriváty pyrimidinu pro aplikaci v OLED, 72. Sjezd chemiků, Praha (Czech Republic), 6.–9. 9. 2020, p. 160.

[4] S. Achelle, M. Fecková, M. Fakis, F. Bureš, J. Rodríguez-López, F. Robin-le Guen: White light emission of pyrimidine chromophores: controlled protonation and long lived intramolecular charge transfer fluorescence, French Swiss Photochemistry Symposium, 21.–22. 21. 2021, online.

[5] S. Achelle, M. Fecková, M. Fakis, J.-P. Malval, F. Bureš, R. Plaza-Pedroche, J. Rodríguez-López, F. Robin-le Guen: The pyrimidine ring: a wonderful platform for the conception of advanced luminescent materials, XXIX European Colloquium on Heterocyclic Chemistry, 26.–28. 6. 2021, online.

Posters:

[1] M. Fecková, S. Achelle, F. Robin-le Guen, P. le Poul, F. Bureš: 2,4-Distyryl and 2,4,6-Tristyrylpyrimidines: Synthesis and Optical Properties, Barrande-Vltava French-Czech Chemistry Meeting, Strasbourg (France), 27. –28. 8. 2018, p. 84.

[2] M. Fecková, S. Achelle, F. Robin-le Guen, P. le Poul, F. Bureš: 2,4-Distyryl and 2,4,6-Tristyrylpyrimidines: Synthesis and Optical Properties, Journee Des Doctorants, Rennes (France), 28. 6. 2018, p. 22.

[3] M. Fecková, S. Achelle, F. Robin-le Guen, P. le Poul, F. Bureš: Synthesis and Photophysical properties of 2,4-Distyryl and 2,4,6-tristyrylpyrimidines, 53rd Advances in Organic, Bioorganic and Pharmaceutical Chemistry „Liblice 2018“, Lázně Bělohrad (Czech Republic), 2.–4. 11. 2018, p. 76.

[4] J. Tydlitát, M. Fecková, S. Achelle: Acid-Responsive Donor-Substituted Triphenylamine Chromophores, 18th International Symposium on Novel Aromatic Compounds, Sapporo (Japan), 21.–26. 7. 2019, p.39.

[5] M. Fecková, F. Bureš: Syntéza push-pull chromoforů s SF_5 akceptorní skupinou, 71. Zjazd chemikov, Vysoké Tatry (Slovakia), 9.–13. 8. 2019, p. 178.