

VILNIUS UNIVERSITY
CENTER FOR PHYSICAL SCIENCES AND TECHNOLOGY

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TUNING OF THE FLUORESCENCE PROPERTIES OF NITROGEN
HETEROCYCLIC COMPOUNDS BY POLAR SUBSTITUENTS

Summary of doctoral dissertation
Material engineering, Technological sciences (08 T)

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LINA SKARDŽIŪTĖ

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Santrauka

Organiniai junginiai vis plačiau taikomi puslaidininkinės optoelektronikos prietaisų technologijose. Organinės elektronikos prietaisai savo efektyvumu ne tik siekia tradicinių puslaidininkinių prietaisų parametrus, tačiau be tradiciniams puslaidininkiams būdingų elektrinių savybių pasižymi ir unikaliomis, plastikams būdingomis ypatybėmis, būtent nedidele kaina, dideliu plotu, lankstumu ir gamybos paprastumu [1]. Spartus technologijų vystymasis nebūtų įmanomas be pažangos naujų organinių medžiagų sintezėje, kur naudojamos vis sudėtingesnės molekulinės sistemos, išsiskiriančios unikaliomis savybėmis. Daugiafragmentės medžiagos su įvairiomis funkcinėmis grupėmis leidžia valdyti organinių darinių elektronines bei fotofizikines savybes, svarbias elektronikos taikymams. Plačias galimybes sintezei ir savybių valdymui atveria heteroatomų įvedimas į π -konjuguotąją sistemą, būdingą cikliniams organiniams junginiams [2]. Optoelektronikos taikymams yra itin svarbu suprasti daugiafragmenčių organinių darinių stuktūros-savybių sąryšius, o organinės sintezės metodų įvairovė atveria itin plačias galimybes valdyti organinių puslaidininkinių medžiagų ir jų prietaisų fotofizikines savybes.

Šiame darbe tiriamos kelios organinių liuminoforų klasės - naujų pirimidino, pirolo[2,3-d]pirimidino ir purinų junginių serijos, išsiskiriančios jautrumu išoriniams poveikiams bei struktūros pokyčiams ir biologiškai aktyviomis savybėmis bei struktūriniu panašumu į DNR fragmentus. Disertacijos tikslas - detaliai ištirti šių azoto heterociklinių darinių liuminescencijos savybes bei išsiaiškinti pastarųjų valdymo mechanizmus modifikuojant junginius įvairaus poliškumo ir morfologijos pakaitais. Taip pat buvo siekiama ištirti naujų junginių taikymo galimybes fluorescenciniam metalų jonų jutimui bei fluorescuojančių nano-agregatų formavimui.

Darbą sudaro keturi skyriai. Pirmasis skyrius pradedamas įvadu, toliau pateikti darbo tikslai ir uždaviniai, darbo naujumas ir ginamieji teiginiai, disertantės, kartu su bendraautoriais, publikuotų mokslinių straipsnių ir konferencijų pranešimų, kuriuose pristatyti disertacijoje pateikti moksliniai tyrimai, sąrašas. Antrąjį skyrių sudaro išsami azoto heterociklinių darinių sandaros ypatybių ir taikymų organinei elektronikai bei fotonikai apžvalga. Jame apžvelgiamas ir azoto heterociklinių junginių biologinis aktyvumas bei taikymai fluorescenciniuose bio-jutikliuose ir žymekliuose.

Trečiasis skyrius apžvelgia naujų azoto heterociklų junginių fluorescencijos savybių valdymą. Skyrius sudarytas iš penkių dalių. Pirmoji nagrinėja izomerinių pirimidino ir karbazolo junginių optines savybes. Ypatingas dėmesys skiriamas polinių pakaitų ir jų jungimo topologijos įtakai junginių fluorescencijos savybėms, taip pat nagrinėjami junginių sužadavimo relaksacijos kanalai bei jiems būdingi solvatiniai efektai. Toliau tiriamas bi-fenil pirolo[2,3-d]pirimidinų darinių fotofizikinių savybių valdymas poliniais pakaitais, taip pat detalai analizuojami junginimas būdingi solvatiniai efektai. Trečiame skyrelyje aprašomos bi-fenilkarbazol pirolo[2,3-d]pirimidinų junginių fluorescencijos ir krūvio pernašos savybės bei analizuojamas polinių karbazolo fragmentų poveikis joms. Ketvirtame ir penktame skyriuje pateiktos pirolo[2,3-d]pirimidino junginių su triazolų fragmentais ir purinų junginių optinės savybės, taip pat analizuojama įvairaus poliškumo ir masyvumo įtaka junginių fluorescencijos savybėms.

Ketvirtojoje disertacijos dalyje tiriami pirimidinų ir pirolo[2,3-d]pirimidinų junginių taikymai, ją sudaro du skyriai. Pirmajame aprašomas fluorescuojančių nanoagregatų formavimas iš pirolo[2,3-d]pirimidino darinių, bei jų fotofizikinių tyrimas, taip pat nagrinėjamas agregacijos nulemtas fluorescencijos stiprinimas. Antrasis skyrius aprašo pirolo-pirimidino ir pirimidino darinių su dimetilamino fragmentais, skirtų fluorescenciniam metalų jonų atpažinimui, tyrimus. Nagrinėjamas fluorescencijos stiprinimas metalų jonais, spalvinis metalų jonų jutimas ir kompleksacijos pagrindinėje būsenoje nulemtas tirpalų sugerties spektrų kitimas.

Kiekvieno tiriamojo skyriaus pabaigoje apibendrinami pagrindiniai rezultatai bei pateikiamos tyrimų išvados. Darbo pabaigoje pateiktas naudotos literatūros bibliografinis sąrašas.

Introduction

The use of organic semiconductors in electronic and optoelectronic devices, such as OLED displays, circuits, organic solar cells and biosensors is constantly increasing. Organic electronic devices benefit from unique characteristics inherent to plastics, namely low cost, possibility to create large area and flexible devices, and more simple manufacturing techniques [1]. Rapid technological development would not be possible without the progress in the synthesis of new organic materials and the use of more complex molecular systems with unique characteristics. Multifragment organic systems with various functional groups enable specific photophysical properties necessary for electronic applications. Moreover, the introduction of hetero atoms into the π -conjugated system of organic cyclic compounds opens ample opportunities for the tuning of their electronic and optical properties. The understanding of the structure-property relations of such organic compounds is of high importance.

In this work several series of novel fluorescent organic systems, distinguished by sensitivity to effects of the surrounding media and structural changes as well as the biological activity and similarity to some DNA fragments, are being investigated.

Aim and tasks of the dissertation

The goal of this dissertation was to carry out a detailed examination of the photophysical properties of novel pyrimidine, pyrrolo[2,3-d]pyrimidine and purine derivatives and to analyze the tuning possibilities of their optical properties by modifying new compounds with substituents of various polarity and morphology. It was also aimed at exploring the opportunities of applications of the new compounds for fluorescent metal ion sensing and formation of fluorescent nano-aggregates. The following tasks were formulated:

- To investigate the variations of the photophysical properties of pyrimidine based derivatives with peripheral carbazole units, induced by the polarity and linking topology of the substituents. To investigate the pattern of the changes in fluorescence efficiency in media of different polarity and to evaluate the dominant processes of the excitation recombination.

- To investigate the possibility of the tuning of photophysical properties of bi-phenyl and bi-phenylcarbazolyl pyrrolo[2,3-d]pyrimidine derivatives by polar substituents. To analyze the impact of intramolecular twisting reactions on their fluorescence properties in various media.
- To assess the impact of polar and steric functional groups on the photophysical properties of novel D- π -A- π -D triazole substituted pyrrolo[2,3-d]pyrimidine systems. To investigate the changes in fluorescence efficiency in media of different polarity and to evaluate the dominant processes of excitation recombination.
- To evaluate the photophysical properties of novel purine derivatives.
- To form fluorescent nano-aggregates based on pyrrolo[2,3-d]pyrimidine compounds and to assess the dependency of their photophysical and morphological properties on the polarity and structure of functional groups.
- To evaluate the fluorescent ion sensing properties of several pyrimidine and pyrrolo[2,3-d]pyrimidine systems.

Novelty of this work

All the organic compounds presented in this work are newly synthesized and their optical and electronic properties have not been previously investigated. Although various pyrimidine and pyrrolo-pyrimidine derivatives are extensively studied as medically active agents, so far their fluorescence properties have been scarcely researched, and there are few published works related to their photophysical properties. This work demonstrates that the nitrogen heterocyclic fragments in conjunction with polar substituents form the intramolecular charge transfer complexes and their fluorescence properties are sensitive to the polarity changes of the surrounding media and the substituents, as well as variation of their morphology and intramolecular twisting. The possibility to form fluorescent nano-aggregates and fluorescent sensing of mercury and iron ions is also presented in this work.

Statements to defend

- Heterocyclic moieties with nitrogen hetero-atoms (pyrimidines, pyrrolo[2,3-d]pyrimidines and purines) in conjunction with donor-like fragments form intramolecular charge transfer complexes, which determine strong positive solvatochromism and enable tuning of the photophysical properties by the polarity, structure and linking topology of the substituents.
- The fluorescence quantum yield of such donor-acceptor systems varies non-monotonically and is determined by two competing mechanisms:
 - the decreasing radiative recombination of excitation rate due to increasing intramolecular charge transfer character of the states
 - the decreasing non-radiative recombination of excitation rates due to possibly reducing intersystem crossing.

The optimization of radiative and non-radiative processes enables to reach a maximum fluorescence quantum yield of 71% for a pyrimidine derivative bearing substituents of low polarity in the media of highest polarity.

- Due to a spectral separation of more than 150 nm between the locally excited and twisting induced intramolecular charge transfer states pyrimidine and pyrrolo[2,3-d]pyrimidine compounds bearing di-methylamine moieties with presence of mercury and iron ions exhibit fluorescence enhancement up to 200 times. This enables selective fluorescence sensing of these two metals against ions of other metals (Ag, Cd, Cu, Co, Ni, Pb and Zn).

Layout of the thesis

The work consists of four chapters. The first chapter begins with an introduction, which is followed by the objectives and tasks of the thesis, its novelty, statements for defending and the list of published scientific articles and conference presentations related to the research of the dissertation. The second section presents a detailed review on the structural properties and related photophysical features of nitrogen heterocycles and their

applications in organic electronic and optoelectronic devices. It also gives an overview of their biological activity and applications in fluorescent bio-sensors and markers.

The third section is focused on the analysis of the fluorescence properties tuning of the novel nitrogen heterocyclic compounds. It consists of five parts. The first part presents the optical properties of isomeric pyrimidine compounds with carbazole units with special emphasis on the impact of polar substituents and their linking topology on the fluorescence properties of compounds. The excitation recombination pathways and characteristic solvatic effects are considered. It is followed by the research on the tuning of the photophysical properties of bi-phenyl pyrrolo[2,3-d]pyrimidine derivatives by polar substituents, and detailed analysis of characteristic solvatic effects. The third section describes the photophysical and charge transfer properties of bi-phenylcarbazolyl pyrrolo[2,3-d]pyrimidine compound. The fourth and fifth sections present the optical properties of the triazole substituted pyrrolo[2,3-d]pyrimidine derivatives and purine and purine derivatives.

The fourth part of the thesis presents the applications of pyrimidine and pyrrolo[2,3-d]pyrimidine compounds, it consists of two sections. The first describes the formation of the fluorescent pyrrolo[2,3-d]pyrimidine based nano-aggregates and their photophysical properties along with the aggregation induced emission. The second section describes the research on the applications of pyrrolo-pyrimidine and pyrimidine derivatives for fluorescent metal ion sensing.

Authors contribution

The author of this thesis prepared the samples and performed the experiments of optical characterization of the materials, analyzed the obtained data of measurements and made the conclusions. The author prepared manuscripts of most of papers and all the conference presentations. Part of results were obtained in collaboration with other laboratories: the chemical synthesis of pyrimidine and pyrrolo[2,3-d]pyrimidine derivatives was performed by the scientific group led by prof. Sigita Tumkevičius, Organic Chemistry department, Faculty of Chemistry, Vilnius University, purine derivatives were synthesized by prof. Maris Turks' group, Material science and applied chemistry faculty of Riga Technical university. Theoretical modeling was performed by

doc. A. Gruodis and Jonas Bucevičius. SEM pictures were made by dr. Simas Šakirzanovas.

III. Tuning of the fluorescence properties of nitrogen heterocyclic compounds

3.1 The impact of polar substituents and their linking topology on the fluorescence properties of isomeric pyrimidine and carbazole derivatives

Owing to strong aromaticity, significant π -deficiency, presence of n- π electronic states, pH sensitivity, and ability of its nitrogen atoms to take part in the chelation processes, pyrimidine, among other azaheterocycles is a desired functional group to be incorporated in more complex organic structures targeted for numerous applications [3]. π -conjugated pyrimidine derivatives are used in organic electronic and optoelectronic devices, such as of OLEDs, sensors, supramolecular assemblies, liquid crystals and dyes for solar cells [4]–[12]. Pyrimidine ring is frequently used in push-pull structures as strong electron-withdrawing unit and together with electron-donating moieties results in intramolecular charge transfer character, which plays an important role in most of the key applications. Carbazole is a well-known electron-donor moiety and possess good hole transporting properties, intense blue luminescence and electroluminescence, rigid structure and enhanced thermal stability. It is also widely used as functional building block in the fabrication of various optoelectronic devices [13]–[16].

This section presents the analysis of the optical properties of novel donor-acceptor-type chromophores based on pyrimidine core and carbazolylphenyl branches at the periphery. The impact of the polarity and linking topology of various aryl substituents on the emission properties is considered. The optical properties of the novel compounds were evaluated by measuring the absorption and fluorescence spectra, fluorescence decay profiles and evaluating fluorescence quantum yields and decay constants of their dilute solutions. The measurements were carried out in several solvents of various polarity. Experimental data were supported by quantum chemical calculations.

The DFT calculations revealed that aryl substituents located at 2- position of the pyrimidine ring are coplanar, whereas the benzene rings at the 4- and 6-positions are slightly out of plane (by dihedral angles from 16° to 23°) with the rest of the molecule. All the derivatives exhibit pronounced intramolecular charge transfer character of the excited states with HOMO orbitals being localized mostly on donor-like carbazolylphenyl branches, while LUMO orbitals cover the pyrimidine core.

Incorporation of the strong electron-donating 4-dimethylaminophenyl group resulted in the localization of the HOMO orbital on this moiety. Large intramolecular charge transfer between the donor-like functional groups and the acceptor-like pyrimidine core manifests itself in the fluorescence properties examined in media of increasing polarity.

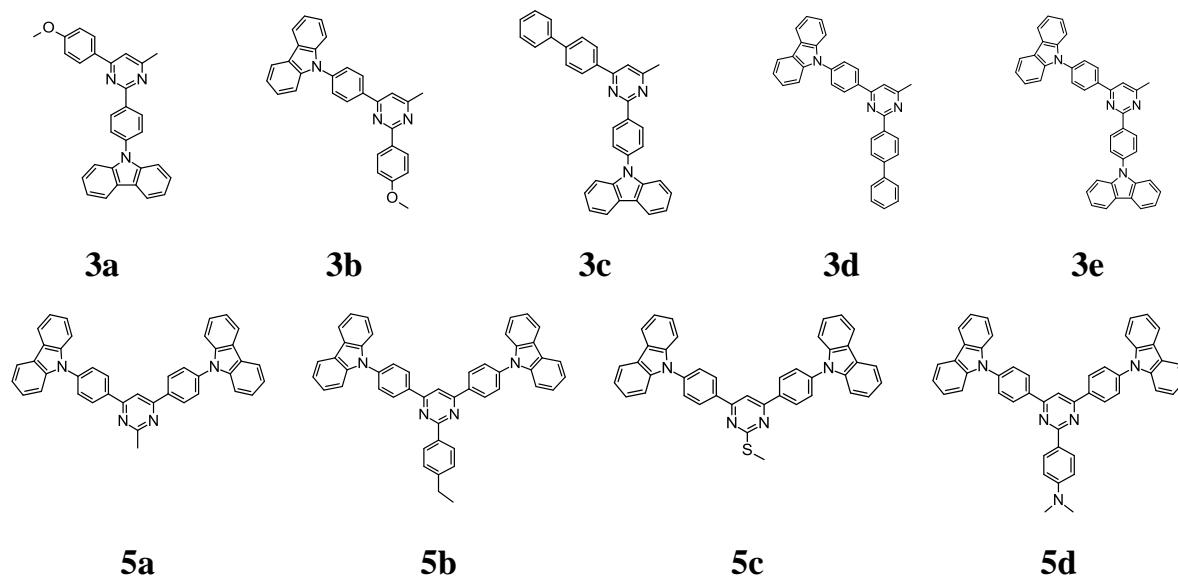


Fig 3.1. Chemical structures of the new pyrimidine derivatives

The optical properties of the new pyrimidine derivatives are presented in Figure 3.2 and summarized in Table 3.1. The UV/vis spectra of the synthesized compounds **3a-e** and **5a-d** in non-polar toluene solution are characterized by several absorption bands positioned in the UV region ($\lambda_{\text{abs}} = 282\text{--}364$ nm) (Table 3.1, Figure 3.2). The absorption bands at 292 nm and 341 nm are characteristic to carbazolyl moieties [17]. This is in line with DFT calculations, which showed the HOMO orbitals to be localized on (carbazolyl)phenyl units. Compound **5d**, bearing strong electron-donating 4-dimethylaminophenyl group at the 2- position of the pyrimidine core, showed distinct changes in the absorbance spectrum with an almost two-fold increase of the intensity of the lowest energy absorbance band, peaking at 354 nm. This band corresponds to the transitions associated mainly with dimethylamino group according to the DFT modeling results.

All the compounds comprising (carbazolyl)phenyl moieties as electron-donating fragments, exhibit strong UV-blue fluorescence, broad structureless spectra with the emission maxima located in a region of 378-410 nm (Table 3.1, Figure 3.2). This is in line with the quantum chemical calculations, which revealed that LUMO orbitals are localized mainly on the pyrimidine core for all the derivatives with slight variation of extension to phenyl fragments.

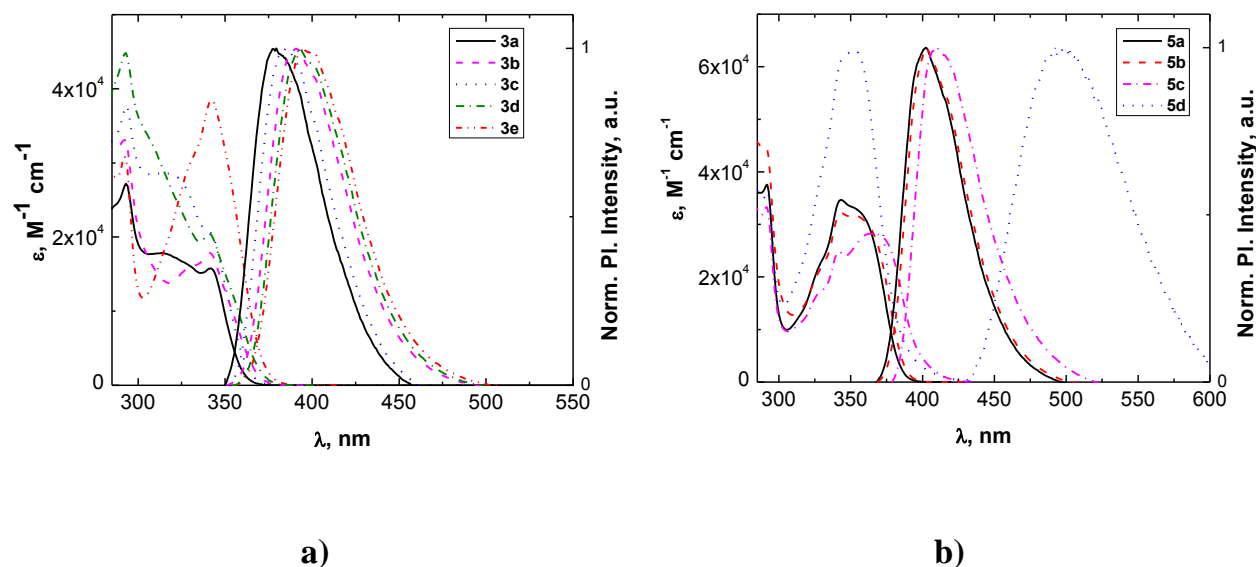


Fig. 3.2. The absorbance and fluorescence spectra of compounds **3a-e** (a) and **5a-d** (b) in toluene.

The fluorescence quantum yield (ϕ_F) values for the synthesized compounds **3**, **5** markedly depend on the nature of aryl branches and their position in the pyrimidine ring. The attachment of the (carbazolyl)phenyl moieties at the 4- position of the pyrimidine ring (compounds **3b** and **3d**) instead of 2- position (compounds **3a** and **3c**) enabled the increase ϕ_F up to 46% for **3b** and 52% for **3d**, respectively. Incorporation of two (carbazolyl)phenyl fragments into 2- and 4- positions of the pyrimidine ring (compound **3e**) resulted in further enhancement of fluorescence quantum yield up to 64%.

To get more insight into the variation of the fluorescence efficiency the radiative and non-radiative excitation decay pathways were examined by studying the luminescence transients of the materials. The decay transients of the synthesized compounds **3**, **5** fitted to single exponential profiles. The estimated values of decay lifetimes in the dilute toluene solutions are summarized in Table 1. The variation of the

non-radiative decay rates is much more prominent than of the radiative decay rates and causes distinct changes in the fluorescence quantum yields of differently linked isomers. Depending on the position of the substituents in the isomeric compounds the non-radiative decay lifetimes vary 2-3 times, from 1.83 ns (compound **3a**) to 3.46 ns (compound **3b**) and from 1.51 ns (compound **3c**) to 4.73 ns (compound **3d**). The attachment of more bulky carbazole group to the 4-phenyl moiety suppresses torsional motions thereby justifying reduced non-radiative decay rate and enhanced ϕ_F for compounds **3b,d**. More rigid structure of the compound **3e**, bearing two electron-donating (carbazolyl)phenyl moieties, leads to the highest quantum yield (64%) and the lowest non-radiative decay rate due to higher suppression of the parasitic intramolecular torsions by more bulky substituents.

Table 3.1. UV/vis and photoluminescence (PL) data of compounds **3a-e** and **5a-d** in toluene solutions.

	Compound	λ_{abs} , nm	λ_{pl} , nm	Φ_{pl} , %	τ , ns	τ_{R} , ns	τ_{NR} , ns
1	3a	292,314, 341	378	34	1.21	3.56	1.83
2	3b	292, 330, 341	390	46	1.87	4.07	3.46
3	3c	293, 316, 341	386	24	1.15	4.79	1.51
4	3d	292, 341	392	52	2.27	4.37	4.73
5	3e	293, 342	398	64	2.44	3.81	6.78
6	5a	286, 291, 343, 355	402	65	2.05	3.15	5.86
7	5b	282, 290, 344, 354	402	71	2.05	2.89	7.07
8	5c	291, 342, 364	410	45	1.45	3.22	2.64
9	5d	292, 353	498	7	7.85	112.14	8.44

A more dramatic (almost two-fold) increase of the non-radiative decay rate resulted in lowering of ϕ_F for compound **5c**, bearing an electron-donating methyl-thio group at the 2- position of the pyrimidine core. The presence of a strongly electron-donating group adversely affects fluorescence quantum yield - compound **5d**, bearing a strong electron-donating 4- dimethylaminophenyl group at 2- position of the pyrimidine

ring, exhibited the longest radiative decay lifetime (112.14 ns) among all the studied compounds, resulting in notable decrease in fluorescence quantum yield to 7% .

Since the pyrimidine compounds exhibited pronounced intramolecular charge transfer character, the solvatochromic behavior of absorbance and emission of compounds **3a-e** and **5a-d** in solvents of different polarity (Toluene, THF, CHCl₃, and DMF) were investigated. The variation of fluorescence spectra maxima, radiative and non-radiative fluorescence lifetimes with increasing polarity of the solvents is represented in Figure 3.3.

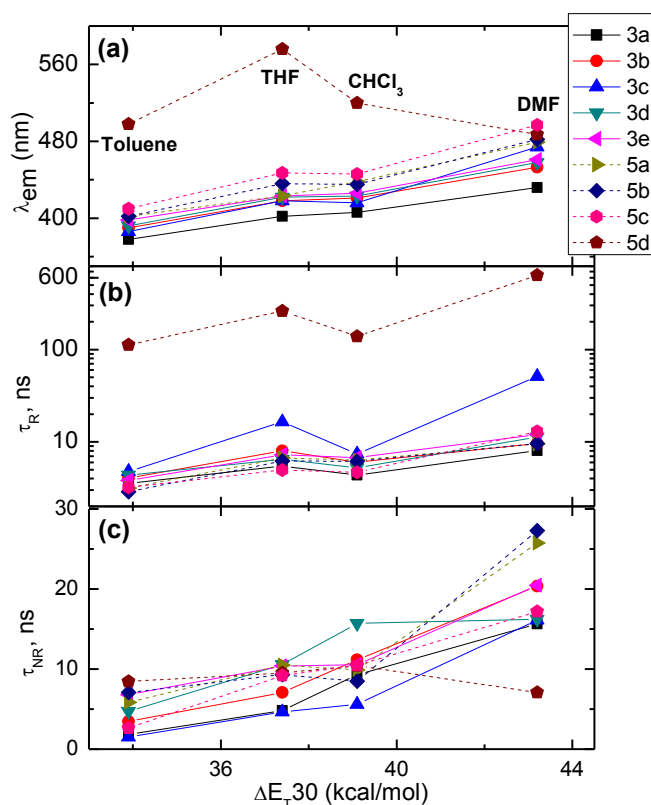


Fig. 3.3. Fluorescence spectra maxima (a), radiative (b) and non-radiative (c) fluorescence decay lifetimes of compounds **3, 5** as a function of Dimroth-Reichardt polarity parameter [18].

The absorption spectra show minor changes with increasing polarity of the solvents revealing insignificant intramolecular interaction between donor and acceptor groups in the ground state. In contrast, the emission spectra exhibit distinct solvent dependence. Broad structureless emission spectra and larger Stokes shifts were observed on increasing solvent polarity, which is typical for solvent stabilized charge transfer states. The common tendency for the studied pyrimidine derivatives is a bathochromic

shift of the emission peaks from 50 nm to 90 nm with increasing solvent polarity. This is typical solvatochromic behavior for compounds that undergo an intramolecular charge transfer upon excitation, leading to a highly polar, charge-separated emitting state stabilized by polar solvents. The most pronounced red shift was observed for compound **3c** ($\lambda_{em} = 386$ nm in toluene and 474 nm in DMF) and compound **5c** ($\lambda_{em} = 410$ nm in toluene and 497 nm in DMF). Compound **5d**, where HOMO orbital is located on 4-dimethylaminophenyl group, showed a distinct solvatochromic behavior which is characteristic for compounds possessing strongly electron-donating dimethylamino group [19].

The increase of the radiative decay lifetimes with increasing solvent polarity is in good agreement with the observed red-shift of the emission spectra and is in accordance with the charge transfer nature of the excited states. Concomitantly, the non-radiative decay lifetimes also increase with increasing solvent polarity. The viscosity of the solvents is similar, thus the decreased non-radiative decay rate cannot be attributed to the hindrance of the intramolecular vibrations. One of the plausible reasons for the decreasing of non-radiative decay rates with increasing solvent polarity could be the increase of the intersystem crossing rate to triplets, which could be altered by changing separation of singlet and triplet energy levels due to the solvent effects [20].

The competition between the radiative and non-radiative processes results in non-monotonous variation of the obtained quantum yields from 24% to 75% depending on the polarity of surrounding media. The highest ϕ_F determined by the longest non-radiative decay and only modest charge transfer character of the excited states were revealed in 4,6-diarylpyrimidines **5a** ($\phi_F = 73\%$) and **5b** ($\phi_F = 74\%$) bearing non-polar substituents at the position 2 of the pyrimidine ring. On the contrary, compound **5d** with markedly stronger charge transfer character of the excited states, showed systematic increase of radiative decay lifetime up to 637 ns, which along with low non-radiative decay lifetime of 7 ns resulted in a poor fluorescence efficiency.

Conclusions

Most of the compounds exhibit efficient UV-blue fluorescence (peaking at 380 - 410 nm) with up to 71% emission quantum yield in non-polar solvents. Emission

properties are strongly affected by the linking topology of the aryl substituents. The highest ϕ_F were attained in the derivatives with two electron-donating (carbazolyl)phenyl fragments and a non-polar substituent at the 2- position of the pyrimidine core.

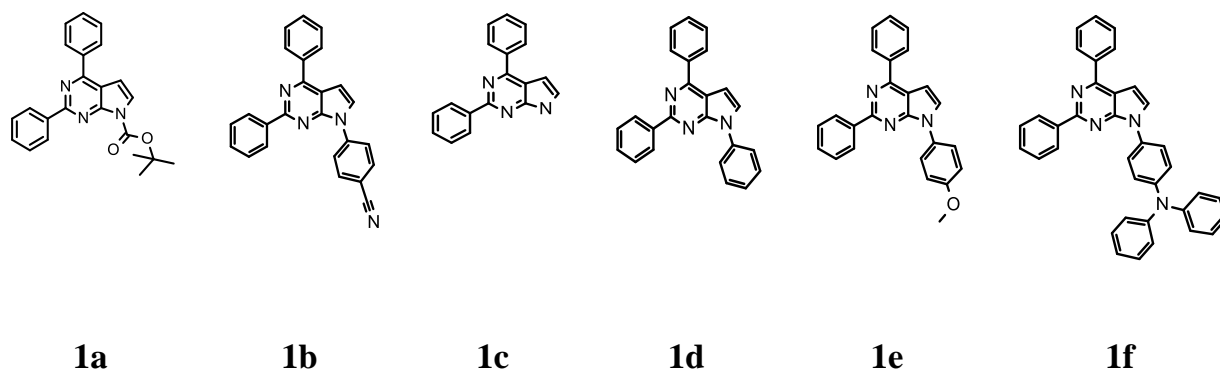
Strong intramolecular charge transfer character of the excited states was revealed. Most of the compounds exhibit positive solvatochromic resulting in a dramatic enhancement of excited state lifetimes (up to 5 times). Non-monotonous variation of ϕ_F was revealed, determined by two competing mechanisms of excitation deactivation, namely the decrease of radiative relaxation rate due to enhanced ICT and the decrease of non-radiative relaxation rate most likely induced by the enhanced intersystem crossing to triplets. The sensitivity of the emission properties to the polarity of the surrounding media could be useful in the applications of pyrimidine derivatives as fluorescent sensors.

3.2 Tuning of the photophysical properties of bi-phenyl pyrrolo[2,3-d]pyrimidine derivatives by polar substituents

The efficiency of organic semiconductors is greatly dependent on the possibility to control the electronic and optical properties of the organic semiconductors via their chemical structure. Effective fluorescence of pyrrolo[2,3-d]pyrimidines has been demonstrated a while ago [21], [22]. But only the recent breakthrough in the synthesis of these compounds via the palladium catalyzed Suzuki cross-coupling reactions allowed the synthesis of a new class of multifragment pyrrolo[2,3-d]pyrimidine derivatives, with the possibility to tune their properties via polar substituents. Similarly to pyrimidines, pyrrolo[2,3-d]pyrimidine moieties also exhibit electron-accepting properties. They are widely investigated due to their bio-medical activity as various antiviral, antibacterial, antitumorous and antifungal activity [23]–[27]. Pyrrolo[2,3-d]pyrimidines share a similar structure with two of the four DNA nucleobases, adenine and guanine. Favourable photophysical properties and biological activity could be useful in the applications of such molecules as fluorescent bio-labels and bio-sensors. An incorporation of a fluorescent pyrrolo[2,3-d]pyrimidine derivative into a specific site of oligoribonucleotide has been already demonstrated [28].

The polarity of the pyrrolo[2,3-d]pyrimidine core implies its sensitivity to specific factors induced by the electronic and structural properties of the substituents as well as the features of the surrounding medium. In this chapter the influence of polar substituents upon the photophysical properties of several pyrrolo[2,3-d]pyrimidine based donor-acceptor-type compounds, causing dramatic changes in their photophysical and electronic properties, is examined. The impact of the intramolecular charge transfer and conformational changes were elucidated by the DFT calculations and supported by the detailed analysis of their absorbance and fluorescence spectra, decay transients, fluorescence quantum yields and decay times in various media. The impact of the functional groups for the photophysical properties of the compounds is considered with special emphasis on intramolecular twisting reactions.

The chemical structures of the new 2,4-biphenyl-pyrrolo[2,3-d]pyrimidine derivatives **1a-f** are presented in figure 3.4. The polarity of the substituents at the pyrrolo nitrogen vary from the most acceptor-like tert-butoxycarbonyl group, to the most donor-like triphenylamine.



3.4 pav. Chemical structure of 2,4-biphenyl-pyrrolo[2,3-d]pyrimidine compounds

Fluorescence properties of the materials have been characterised by measuring their absorbance and fluorescence spectra as well as their decay transients in various media. The quantum yields and decay lifetimes in dilute and solid states have been determined. The molecular properties of the compounds have been tested in dilute solutions of various polarity solvents. The impact of intramolecular twisting has been examined by incorporation of the molecules in the rigid polystyrene surrounding.

The origin of the electronic states and the impact of intra-molecular twisting on the optical properties of the molecules were revealed by quantum chemical calculations of the pyrrolo[2,3-d]pyrimidine compounds. Intramolecular charge transfer character for all the derivatives is observed along two axes: (1) along the pyrrolo[2,3-d]pyrimidine core and 2- phenyl fragment and (2) from the substituent at the pyrrolo nitrogen atom to the 4- phenyl moiety. The charge transfer state for the compounds bearing acceptor-like substituents is less prominent. Compound **1e**, with strong donor triphenylamine group showed the most prominent charge transfer with HOMO orbital localized on the triphenylamine group, and LUMO on the pyrrolo[2,3-d]pyrimidine core.

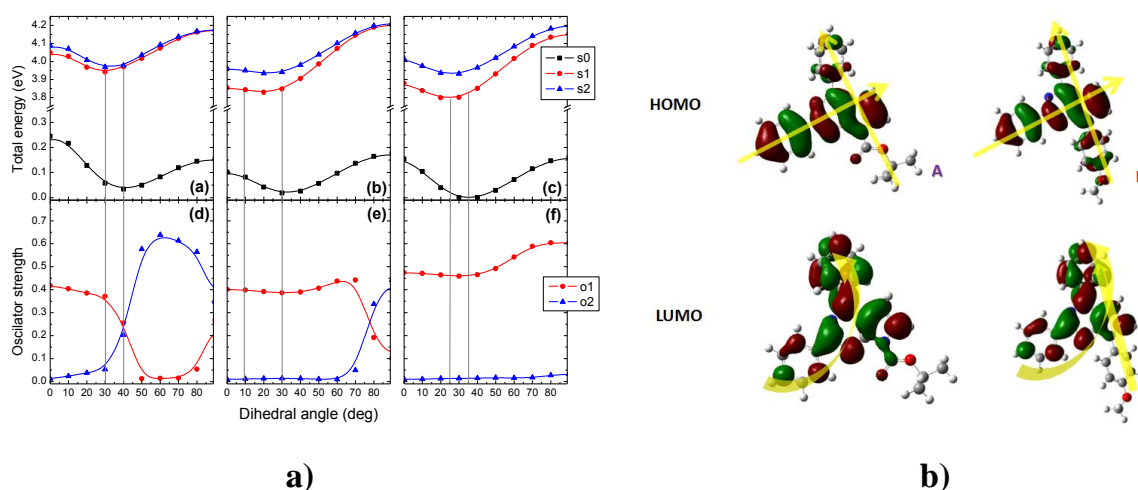


Fig. 3.5 a) Total energies and oscillator strengths at different dihedral angles between 2-phenyl ring and pyrrolo-pyrimidine core in the compounds **1a** (a,d), **1c** (b,e) and **1f** (c,f) and **b)** HOMO and LUMO orbitals of compounds **1a** and **1f**.

Dihedral angles between the different fragments of the molecules have been estimated. The rotation of the phenyl ring attached at the 2- position of the pyrimidine ring was found to be planar with the pyrrolo[2,3-d]pyrimidine plane in both ground and excited states in all the derivatives. The second phenyl fragment at the 4- position of the pyrimidine ring is twisted with respect to pyrrolo-pyrimidine plane in all the derivatives owing to its sterical hindrance and has an adequate energy barrier limiting its planarization. The total energies and oscillator strengths for the lowest singlet transitions are depicted in figure 3.5. Most likely S_1 energy level corresponds to π - π transition, while S_2 represents n - π transition. In the case of compound **1a** these two states are mixed and

depend on the 2- phenyl twisting angle. In the more planar conformation π - π transition is dominating, while n- π is more prominent in the twisted conformation. The addition of more donor-like moieties leads to the parting of the two states.

The fluorescence spectra of dilute THF solutions of compounds **1a-f** are broad and structureless and show a steady bathochromic shift, which systematically coincides with the shift of substituent polarity from the most acceptor-like to the most donor-like and justifies the intramolecular charge transfer character of the excited states. The highest quantum yields (30%) were exhibited by compounds **1c** (without any polar substituent) and **1d** (with weakly polar phenyl moiety). The increase of substituent polarity in both extremities resulted in an almost ten-fold of ϕ_F to 3.6% (compound **1a**) and 3.9% (compound **1f**). The calculated radiative and non-radiative decay lifetimes both show a steady increase with the variation of substituent polarity from acceptor to donor substituents.

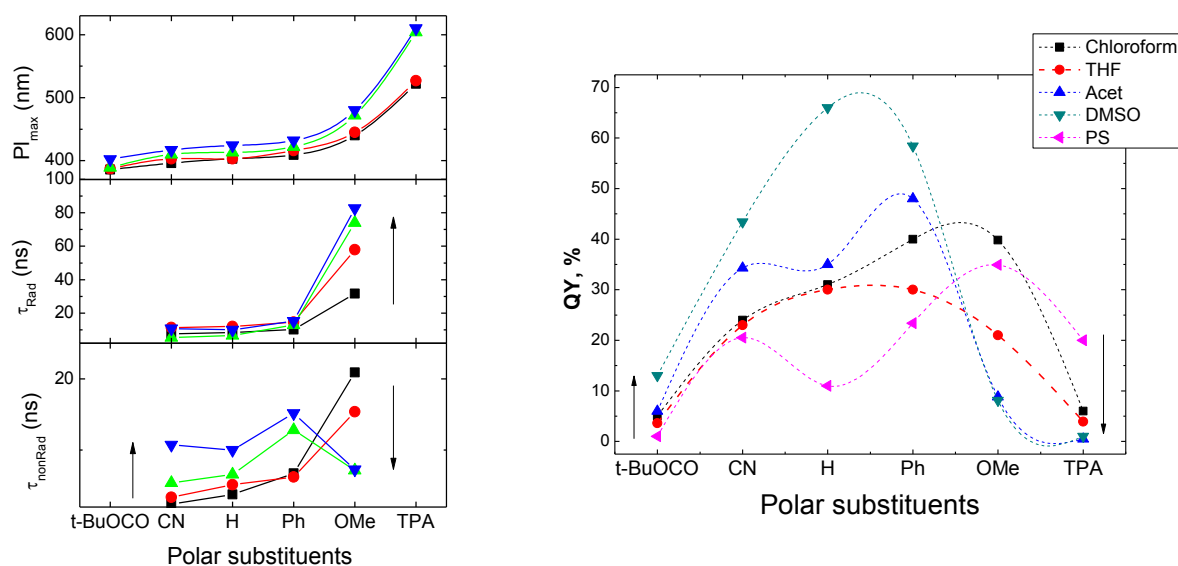


Figure 3.6 Fluorescence spectra maxima, radiative and non-radiative fluorescence decay lifetimes and fluorescence quantum yields of the compounds **1a-f** in solvents of increasing polarity. Lines serve as guidelines for the eye.

Detailed analysis of the fluorescence properties of compounds **1a-f** were performed in solvents of various polarity (chloroform, THF, DMSO and acetonitrile). Fluorescence properties of compounds **1a-f** in different solvents are shown in figure 3.6. All the compounds exhibit bathochromic shifts with increasing solvent dipole moment.

Quantum yields of the derivatives non trivially depend on the polarity of the substituents and the surrounding media. The largest ϕ_F are characteristic to compounds with almost neutral substituents in the media of highest polarity (up to 60%). The radiative decay lifetimes show noticeable increase for more donor-like substituents and with the increase of the solvent polarity. Non-radiative decay lifetimes correlate with the fluorescence quantum yield, showing increase with more neutral substituents and decrease with donor-like moieties. The increase of the radiative decay rate is determined by the increasing intramolecular charge transfer character, due to more prominent solvation shell and the non-radiative decay rates are more affected by the polarity and structure of the substituents. Most likely, the reduction of the non-radiative decay rates can be attributed to the lower intersystem crossing rates.

Conclusions

Intramolecular charge transfer character of the excited states of pyrrolo[2,3-d]pyrimidine derivatives leads to the sensitivity of their fluorescence properties to the polarity of the substituents and surrounding media. Fluorescence efficiency is influenced by two competing mechanisms: (1) the decrease of the rate of non-radiative relaxation due to intersystem crossing controlled by the intramolecular twisting and (2) enhancement of the intramolecular charge-transfer reaction reducing the radiative decay rate with increased polarity of the attached fragments and surrounding media. The highest fluorescence quantum yield can be achieved by substituting pyrrolo[2,3-d]pyrimidines with small conjugated moieties of low polarity in the media of highest polarity. In these conditions polar substituents lead to reduced intersystem crossing rate and moderate intersystem crossing rate sustains higher radiative decay rates in comparison with the non radiative decay rates.

3.3 Tuning of the photophysical properties of bi-phenylcarbazolyl pyrrolo[2,3-d]pyrimidine derivatives

In order to enhance the fluorescence efficiency and to improve the charge transfer properties of the pyrrolo[2,3-d]pyrimidine compounds a series of new derivatives with

the same substituents at the pyrrolo nitrogen position and additional carbazole fragments at the 2- and 4- phenyl rings was synthesized. Fluorescence properties of the dilute THF solutions of the materials have been characterised by measuring their absorbance and fluorescence spectra as well as their decay transients and by calculating their quantum yields and decay lifetimes. In addition to fluorescence measurements, DFT calculations have been performed. The chemical structures of the new derivatives are presented in figure 3.7.

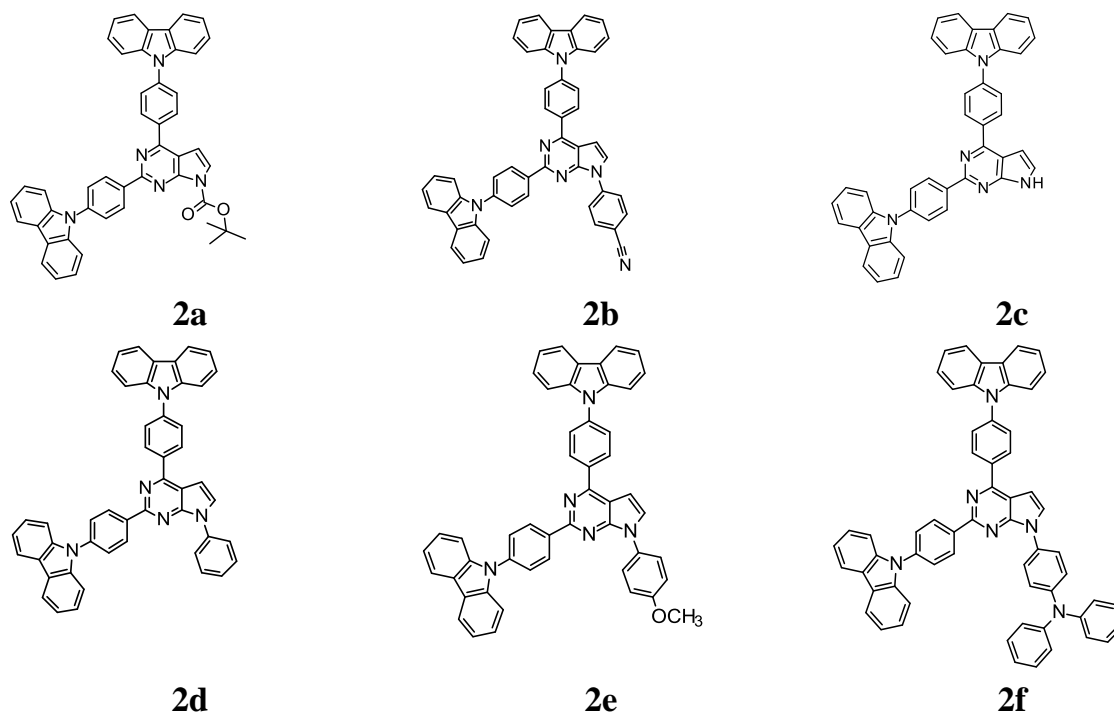


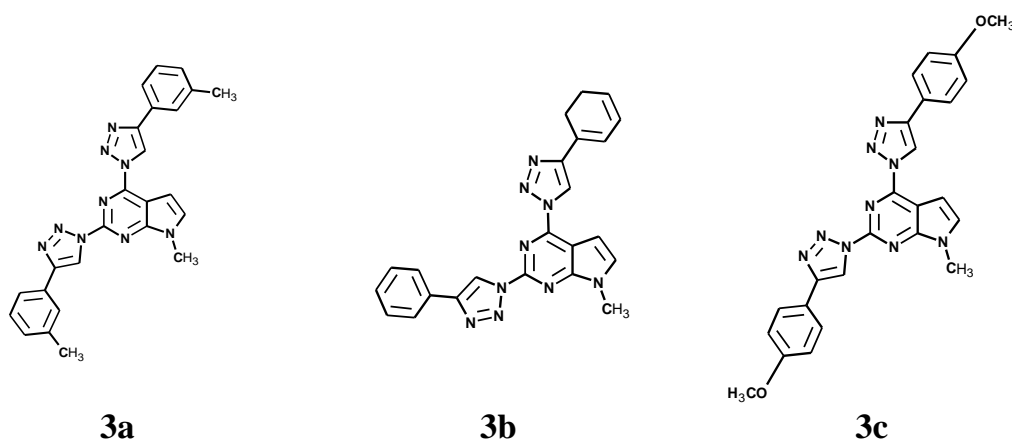
Fig. 3.7. Molecular structures of compounds **2a-f**.

The addition of the electron-donor carbazole units resulted in a much more evident intramolecular charge transfer character of the excited states, with HOMO orbitals localized on one of the carbazole branches (with an exception of **2f**, where HOMO is located on the triphenylamine moiety exhibiting stronger electron-donor nature than carbazoles), while LUMO orbital is located on the pyrrolo[2,3-d]pyrimidine core for all the derivatives. The addition of the carbazole moieties also resulted in the extended π -conjugation of the molecules. Polar carbazole units act similarly as the substituents at the pyrrolo nitrogen by separating the π - π and n - π states in the equilibrium configuration of the molecules. Stronger ICT character results in enhanced fluorescence quantum yields for compounds with the acceptor-like substituents at the

pyrrolo nitrogen. Compound **2a** demonstrates an almost 20-fold increase of ϕ_F up to 67% in comparison with **1a**. However, the addition of donor-like substituents results in reduced fluorescence quantum yields due to elongated radiative decay rates, determined by strong intramolecular charge transfer.

3.5 Optical properties of pyrrolo[2,3-*d*]pyrimidine derivatives with triazole units

This chapter is focused on the analysis of the photophysical properties of new D- π -A- π -D chromophores that contain pyrrolo[2,3-*d*]pyrimidine system as electron-attracting part, triazole linkers and substituted aromatic moieties as the electron-donating parts. Various 1,2,3-triazoles have found application in the fields of bio-conjugation, material science, chemical sensors and drug discovery [29]–[35]. Continuing the research of the previously analyzed pyrrolo-pyrimidine derivatives, novel fluorescent pyrrolo[2,3-*d*]pyrimidine derivatives with a 1,2,3-triazole linker between the aromatic side chains and heterocyclic scaffold have been synthesized. In the current literature triazolylpyrrolo[2,3-*d*]pyrimidines have received very little attention. The impact of the polar and steric substituents on the photophysical properties of the synthesized D- π -A- π -D chromophores were assessed by thorough analysis of their optical and electrochemical properties in various surroundings and the results of DFT modelling. Substituent induced altering of the excited state recombination pathways is discussed with special emphasis on the enhancement of fluorescence efficiency. The molecular structures of the new derivatives are presented in figure 3.8.



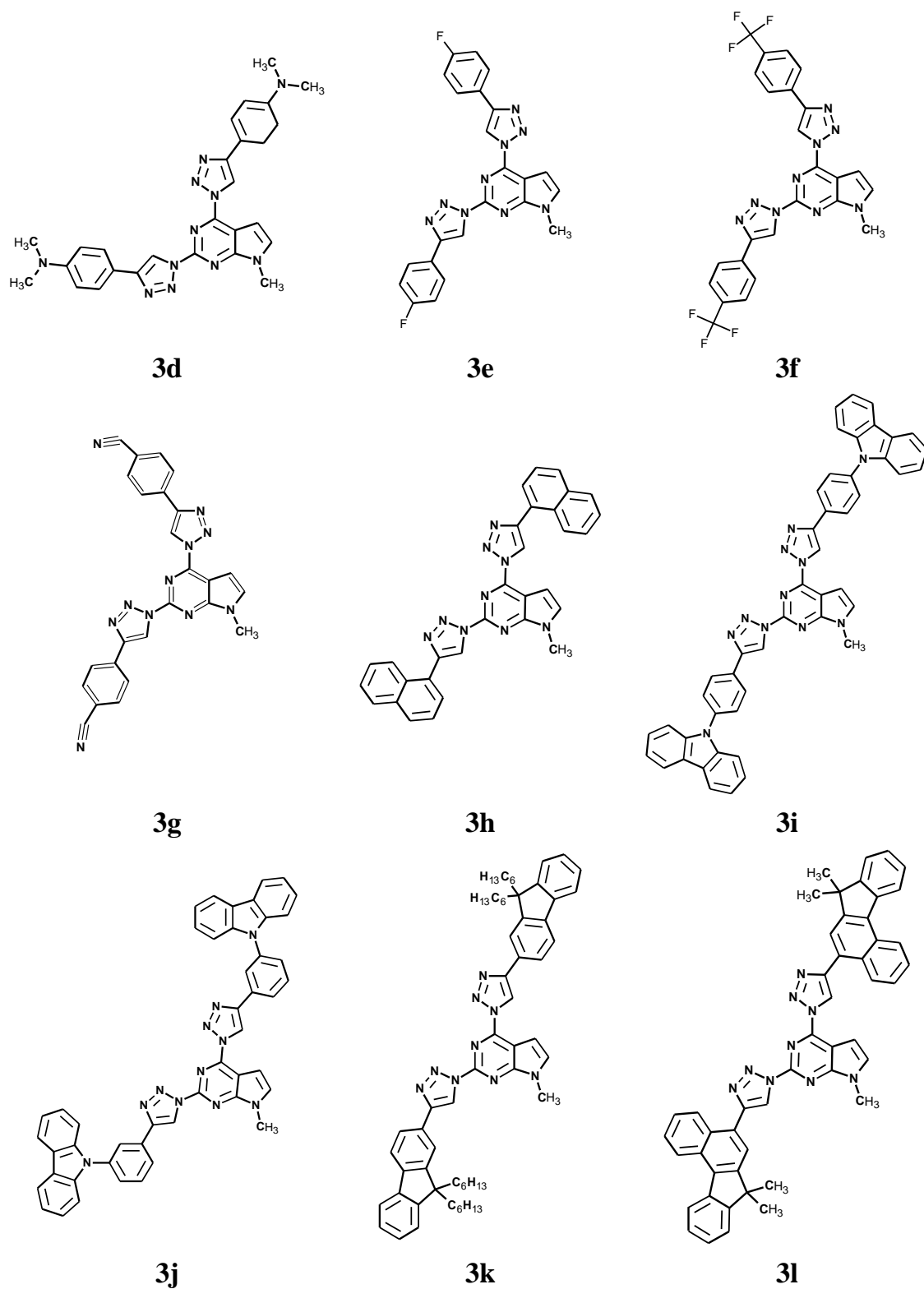


Fig. 3.8 Molecular structures of the pyrolo-pyrimidines with triazole moieties

Examination of geometry of the optimized structures of the studied systems revealed that compounds possessing phenyl substituent at 1,2,3-triazole linker are almost coplanar (**3a-g**, **3k**), while compounds with more bulky aryl fragments exhibit

twisted geometry. A comparison of electronic structures revealed that the LUMO of all the homologues is localized on pyrrolo[2,3-*d*]pyrimidine core involving conjugated coplanar 1,2,3-triazolyl moieties. For molecules possessing small slightly electron-donating substituents (**3a-b**) or electron-withdrawing substituents (**3e-g**) HOMO is localized over the entire molecule, enclosing the pyrrolo[2,3-*d*]pyrimidine core. Introduction of substituents with increasing electron-donating properties (**3c-d**) results in enhanced intramolecular charge transfer. The strongest intramolecular charge transfer character was inherent to molecules with bulky and twisted fragments, showing non-symmetric localization of the HOMO orbitals on the sole substituent attached at the 4- position of the pyrrolo-pyrimidine moiety.

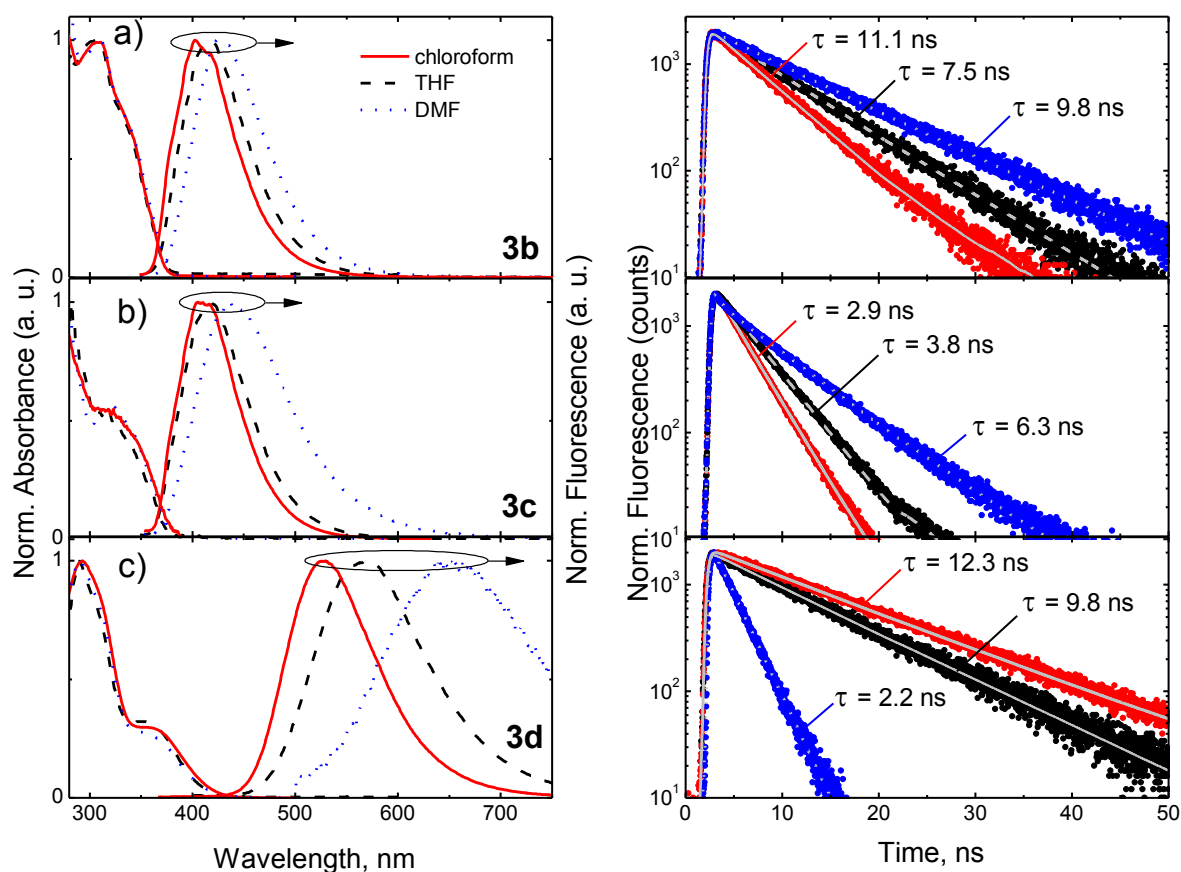


Fig. 3.9. Absorption and fluorescence spectra (left) and fluorescence τ decay profiles (right) of compounds **3b** (a), **3c** (b) and **3d** (c) in dilute chloroform, THF and DMF solutions ($c = 10^{-5}$ M).

The results of absorption and fluorescence spectroscopy, fluorescence lifetime and fluorescence quantum yield measurements in CHCl_3 , THF and DMF solutions of 2,4-bis(4-aryl-1,2,3-triazol-1-yl)pyrrolo[2,3-*d*]pyrimidines (**3a-l**) are collected in Table

3.2. Figure 3.9 shows the normalized absorption and fluorescence spectra of compounds **3b-d** in CHCl₃, THF, DMF. All compounds possessing polar phenyl fragments show broad structureless fluorescence spectra in the region from 402 nm to 649 nm depending on the electronic nature of the substituents and the polarity of the surrounding media. The broadening of the fluorescence spectra and enhanced Stokes shift from 91 nm (**3b** in CHCl₃) to 165 nm (**3d** in CHCl₃) of the fluorescence spectra is due to the strong charge transfer character of the excited states. In accordance with the CT nature of the transitions the enhancement of surrounding media polarity results in even higher red-shift of the fluorescence spectra up to 650 nm and increased Stokes shift – 279 nm.

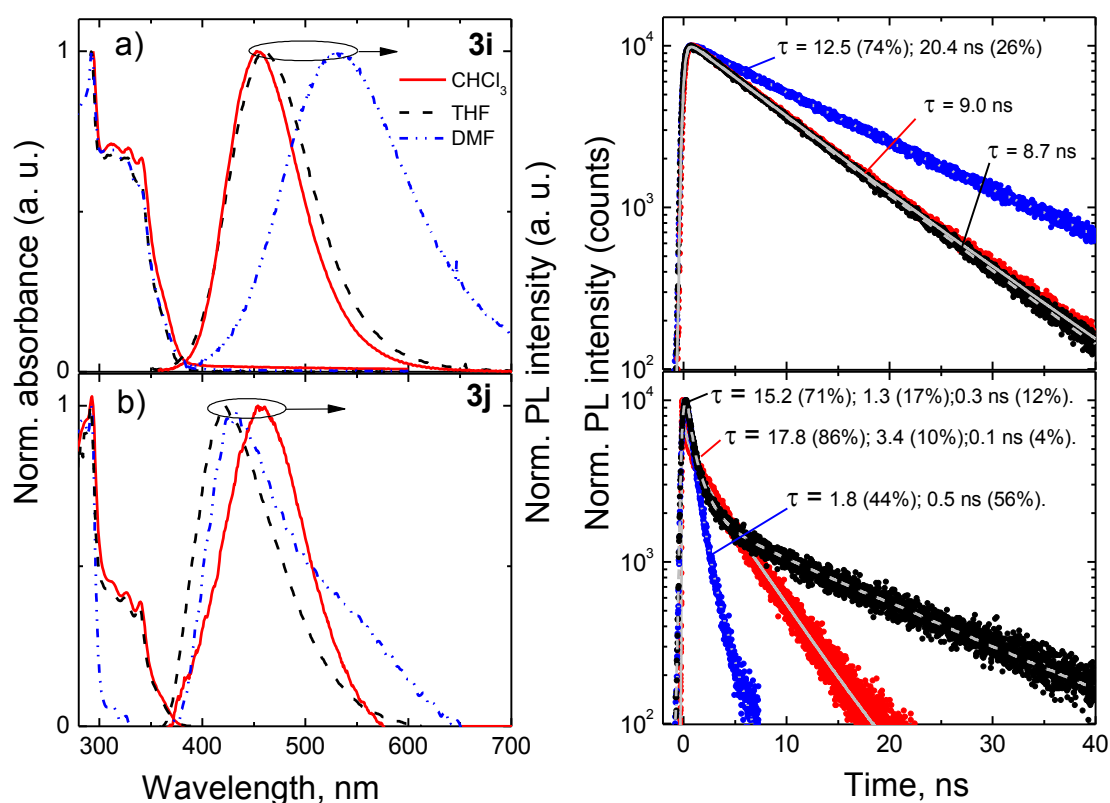


Fig. 3.10. Absorption and fluorescence spectra and fluorescence decay profiles of compounds **3i** (a) and **3j** (b) in dilute chloroform, THF and DMF solutions ($c = 10^{-5}$ M).

Compounds **3h**, **3k** and **3l** bearing naphthyl, fluorenyl and benzofluorenyl fragments-show steady red-shifting of the fluorescence bands from 402 nm to 459 nm in the solvent of low polarity, due to extension of π -conjugated system. All these compounds show minor solvatochromic changes with increasing polarity of the surrounding media. Compound **3i**, bearing bulky electron donating carbazole moiety, shows red-shifted broad fluorescence band at 453 nm in chloroform and at 530 nm in

polar DMF. Interestingly, its isomer - compound **3j**, bearing carbazole fragment at the *meta*-position of the benzene ring, reveals the dual-fluorescence properties in polar DMF surrounding showing both locally excited band at 435 nm, typical for non-polar media, and an additional CT band at around 550 nm (Figure 3.10).

Table 3.2. Optical properties of compounds **3a-l**.

	3a	3b	3c	3d	3e	3f	3g	3h	3i	3j	3k	3l	
CHCl ₃	$\lambda_{\text{abs, nm}}$								247	253			
									293	293	245	246	
	$\lambda_{\text{em, nm}}$	255	264	268	308	249	253	277	245	313	314	293	334
		309	311	318	365	312	310	311	298	329	326	319	348
	$\Phi_{\text{F, \%}}$									341	340		
										453	454	422	459
	Stokes shift, nm	52	49	27	52	49	44	52	27	55	6	34	28
		93	91	87	165	91	93	97	106	112	114	103	111
	τ , ns	10.0	11.1	2.9	12.3	11.9	15.3	12.4	12.8	9.0	17.8 (86%) 3.4 (10%) 0.1 (4%)	2.6	3.3
	τ_{R} , ns	10.9	10.7	8.7	23.6	11.4	12.0	13.4	4.7	16.4	-	7.6	11.9
τ_{NR} , ns	10.0	11.1	4.2	25.6	11.9	15.3	12.4	12.8	20.0	-	3.9	4.6	
THF	$\lambda_{\text{abs, nm}}$								249	251			
									295	295	246	246	
	$\lambda_{\text{em, nm}}$	256	262	266	310	250	255	270	247	312	312	293	334
		309	309	321	366	312	312	290	297	324	328	320	348
	$\Phi_{\text{F, \%}}$									342	341		
										459	422	417	455
	Stokes shift, nm	55	73	31	38	61	43	67	32	50	17	32	25
		107	108	97	203	106	110	132	121	117	81	97	107
	τ , ns	7.3	7.5	3.8	9.8	7.8	7.8	7.5	5.5	8.7	15.2 (71%) 1.3 (17%) 0.3 (12%)	3.0	3.7
	τ_{R} , ns	13.2	10.3	12.2	25.9	12.8	18.2	11.1	17.1	17.6	-	9.3	14.8
τ_{NR} , ns	16.1	27.8	5.5	15.9	20.0	13.7	22.8	8.0	17.6	-	4.4	4.9	
DMF	$\lambda_{\text{abs, nm}}$								298	297			
									315	316	295	335	
	$\lambda_{\text{em, nm}}$	311	311	320	309	311	314	279	299	330	326	324	348
					370			312		345	346		
	$\Phi_{\text{F, \%}}$									530	435	436	492
										27	5	41	19
	Stokes shift, nm	71	62	21	3	56	50	56	31	185	89	112	144
		113	112	116	280	120	122	123	133				
	τ , ns	7.3	9.8	6.3	2.2	10.4	10.6	9.8	7.7	12.5 (74%) 20.4 (26%)	1.8 (44%) 0.5 (56%)	6.3	4.8
	τ_{R} , ns	10.2	15.8	30.2	75.0	18.5	21.2	17.6	24.9	-	-	15.4	25.5
τ_{NR} , ns	25.1	25.8	8.0	2.3	23.6	21.2	22.3	11.2	-	-	10.7	6.0	

Most of the compounds demonstrated efficient blue fluorescence with quantum yields up to 71%. Compounds bearing neutral and electron-withdrawing substituents

(**3a-b**, **3e-g**) demonstrated fluorescence quantum yields varying from 44% to 52% in solvent of low polarity (CHCl_3), while the higher polarity of the surrounding media results in slightly higher efficiencies from 50% to 71%. The single exponential profiles of the decay transients enabled the estimation of radiative and non-radiative decay lifetimes. The prominent variation of both radiative and non-radiative decay lifetimes indicates on charge transfer induced intramolecular twisting reactions, determined by solvation shell [19]. Compounds **3c** and **3d** bearing electron donating substituents exhibit more than 3-fold increase of the radiative decay lifetimes in the solutions of polar DMF, while in the case of compounds with non-polar and electron withdrawing moieties, with less pronounced CT nature, the increase of the radiative decay lifetime was about 30%. The non-radiative decay rates are 2 or 3 times higher in the polar surrounding for all the compounds, with the exception of dimethylamino group bearing compound **3d**, where the non-radiative decay rate undergoes a 10-fold increase in polar surrounding. Compounds **3h-k** bearing non-polar bulky aryl substituents revealed similar trends of solvent polarity dependencies of the radiative and non-radiative decay rates. Incorporation of electron donating carbazole units at the *para*-position of the phenyl fragments (compound **3i**) results in the fluorescence quantum yield of 55%, which decreases to 27% in polar surroundings. Interestingly, the attachment of the carbazole unit at the meta position of the phenyl fragment (compound **3j**) results in a dramatic decrease of the fluorescence efficiency to 6%, which might be attributed to the broken symmetry of donor and acceptor moieties, resulting in dual-fluorescence nature of the excited states, prominent not only in the fluorescence spectra but also in the non-exponential decay transients in both non-polar and polar surrounding media.

Conclusions

The synthesized compounds demonstrates efficient blue fluorescence in the range from 400 nm to 450 nm. The DFT calculations revealed that the core of the all the derivatives consists of pyrrolo[2,3-d]pyrimidine moiety and includes triazole fragments, leading to the extension of the LUMO state and enhanced electron-acceptor properties. The bulky aryl substituents show mostly electron donor character and determines the HOMO state. Tuning of the size, polarity and geometry of the substituents alters the

charge transfer character of the transitions, influencing the spectral properties of the fluorescence spectra and fluorescence quantum yield. Intramolecular charge transfer has much influence on the dynamics of radiative and non-radiative decay in polar surroundings. Both processes slow down and the competition between the radiative and non-radiative decay pathways results in smaller fluorescence quantum yields for compounds possessing polar substituents or substituents with twisted geometry. The highest quantum yield of 73% is achieved for a pyrrolo[2,3-d]pyrimidine derivative with small neutral substituents in polar surrounding medium.

IV. Applications of pyrimidine and pyrrolo[2,3-d]pyrimidine compounds

4.1 Fluorescent nano-aggregates based on pyrrolo[2,3-d]pyrimidine derivatives

Molecule arrangement and intermolecular interactions result in special electronic, optical, and chemical features of bulk materials in comparison of single molecules. Recently, much attention has been drawn to organic nanoparticles due to their unique optical and electrochemical characteristics [36]–[38]. The research of the organic nanoaggregates is mainly focused on the structure-property relations of the aggregated nanostructures. A variety of nanoparticle applications is implied by the possibility to tailor electronic and optical nanoparticle properties via chemical engineering of the constituent molecules, as well as an abundance of organic synthesis methods for altering molecule structure. Organic nanoparticles have already been proven to perform well not only in the areas of photovoltaics, organic light-emitting diodes, and field-effect transistors, but also in chemical or biological applications, such as fluorescent labels and sensors [39]–[47].

A special class of organic nanoparticles are the fluorescent organic nanoparticles (FONs) distinguished by high fluorescence efficiency. The molecules forming FONs are usually weakly or non-fluorescent in the isolated state due to the efficient nonradiative

deactivation occurring via intramolecular torsions, while the suppression of these motions in the aggregated state leads to an effective fluorescence turn-on [48]. The fluorescence enhancement phenomenon in the aggregated form is termed aggregation induced emission (AIE) [48]–[50]. The non-planar molecules bearing bulky peripheral groups can constitute amorphous-like aggregates with significantly weakened intermolecular interactions, and thus, can promote AIE property [51], [52].

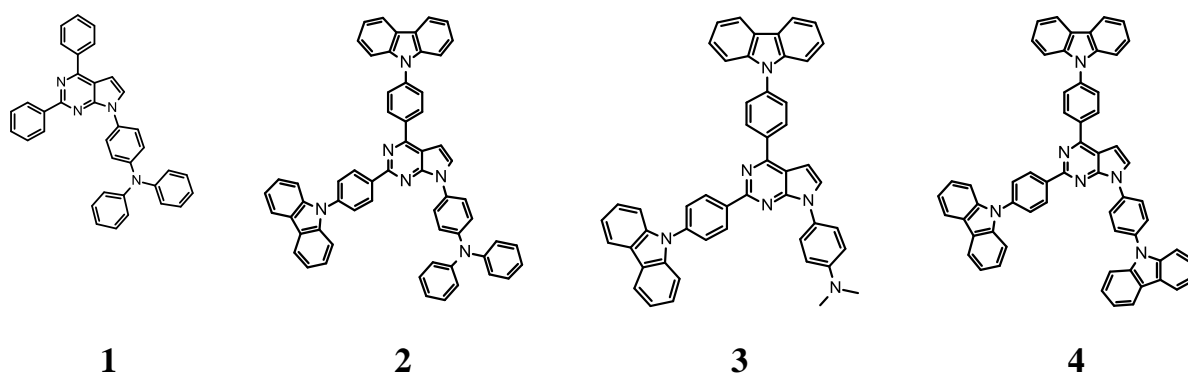


Fig 4.1. Molecular structures of the selected pyrrolo[2,3-d]pyrimidine derivatives for the formation of nanoparticles

In this chapter, the formation and photophysical properties of the FONs based on pyrrolo[2,3-d]pyrimidine derivatives are investigated. The formation of the pyrrolo[2,3-d]pyrimidine-based FONs was performed by the reprecipitation method in aqueous solution. Four derivatives with pyrrolo[2,3-d]pyrimidine core, yet different bulky 4-(diphenylamino)-, 4-(dimethylamino)- or 4-(9-carbazolyl)phenyl end groups were chosen for the research. The photophysical and morphological properties of the fluorescent nanoparticles were examined and compared utilizing absorption and fluorescence spectroscopy, excited state decay time and quantum yield evaluation methods as well as scanning electron and fluorescence microscopy.

Fig. 4.1 shows the chemical structures of the four pyrrolo[2,3-d]pyrimidine derivatives. DFT calculations showed that different (diphenylamino, dimethylamino or carbazolyl) end-groups cause different molecular conformations, thus influence packing morphology of the formed nanoaggregates. Moreover, the end-groups can also exhibit intramolecular torsions/vibrations, and thus, greatly affect photophysical properties of the compounds in dilute solutions. Compounds **1**, **2**, and **3** having flexible phenyl end-

moieties demonstrated low PL QY (1e4%) in the dilute THF solutions accompanied by typical nanosecond (compounds **2** and **3**) or subnanosecond (compound **4**) excited state lifetimes. The inhibition of the intramolecular torsions upon dispersing the compounds in PS matrices resulted in a large enhancement of the PL QYs up to 20-28% and in a noticeable elongation of the average τ due to the reduced nonradiative decay.

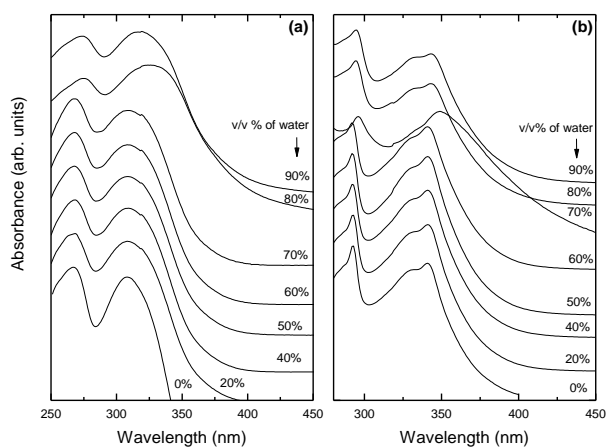


Fig. 4.2. Absorption spectra of the pyrrolo[2,3-d]pyrimidine compounds **1** (a) and **3** (b) in THF/water mixtures with increasing volume percent (v/v%) of water. The spectra are normalized and vertically shifted for clarity.

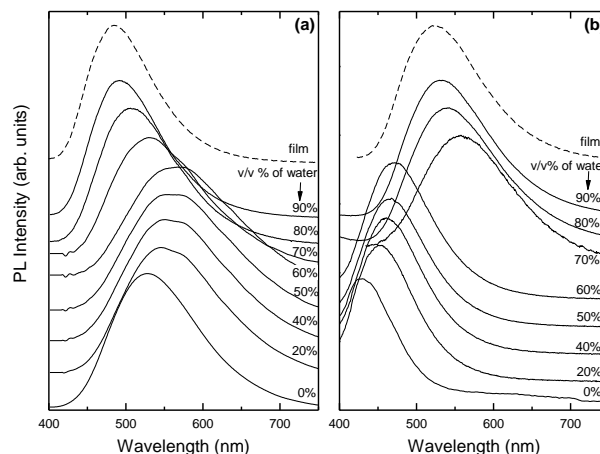


Fig. 4.3. PL spectra of compounds **1** (a) and **3** (b) in THF/ water mixtures with increasing volume percent (v/v%) of water. Dashed curves mark PL spectra of the neat films.

Formation of the pyrrolo[2,3-d]pyrimidine nanoaggregates with increasing water fraction in THF/water mixtures with solute molecules was optically monitored by measuring absorption and PL spectra, PL QY, and PL transients. Fig. 4.2 shows the evolution of absorption spectra of compounds **1** and **3** with increasing water content in the THF/water mixtures. All the derivatives exhibited noticeable changes in the absorption spectra with the water content above 60-0%, whereas below this value, the spectra were dominated by only single molecule features.

Fig. 4.3 depicts PL spectra dynamics of the compounds **1** and **3** with increasing water content in the THF/water mixtures. Generally, the PL spectra of all the pyrrolo[2,3-d]pyrimidine derivatives were mainly dominated by one structureless fluorescence band, which broadened and red-shifted with increasing water fraction up to 60%. The red shift and broadening can be explained by the solvatochromic effect evoked

by changing the THF and water ratio (and thus polarity) in the mixture. Since there were no drastic changes in the shape of the PL spectra of all the derivatives **1-4** as compared to that observed in pure THF, it is safe to assume that the pyrrolo[2,3-d]pyrimidines retained their molecular characteristics in the mixtures up to 60% water. Sudden changes in the dynamics of the PL spectra appeared only when water content exceeded the critical value of 60-70% the, manifesting an emergence of the new aggregated phase.

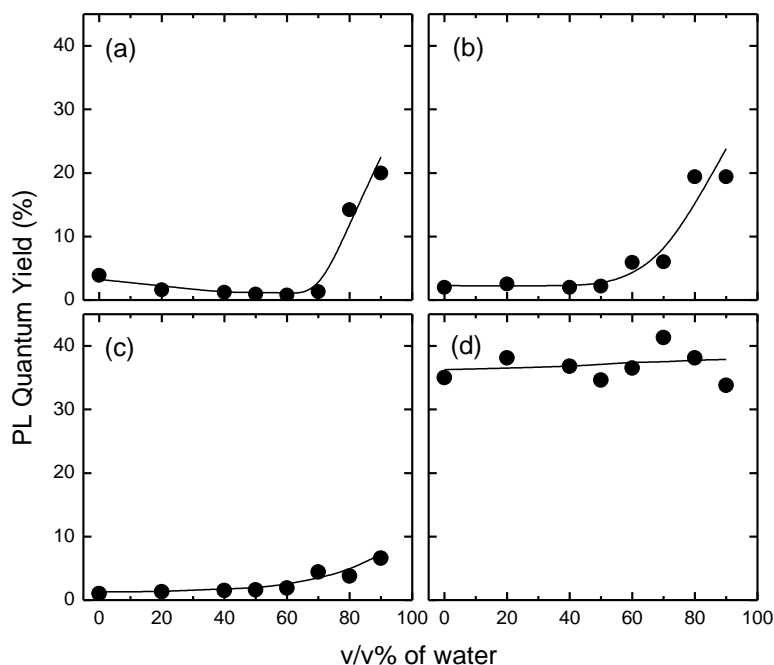


Fig. 4.4. Fluorescence quantum yield of the compounds **1** (a), **2** (b), **3** (c), and **4** (d) in THF/water mixtures with increasing volume percent (v/v%) of water. Lines serve as guides for the eye.

Further evidence for the newly arisen phase is the enhancement of the PL QYs just above the critical water fraction 60-70% (Fig. 4.4). The observed enhancement of the PL QY just above 60% of water fraction occurring concomitantly with the drastic changes in the absorption and PL spectra dynamics is attributed to the suppression of intramolecular torsions due to molecule aggregation. Compound **2** demonstrated a steep increase of the PL QY from 1% up to 20% with increasing water fraction up to 90%, thus delivering the maximal QY turn-on ratio of 20. Particularly, the QYs of the fluorescent aggregates of compounds **1** and **2** are nearly the same as those of their dilute dispersions in PS matrices signifying an absence of special molecule arrangements in the aggregates. Most likely, the molecules in these aggregates pack in a random way with a

relatively large average intermolecular distance, and thus, relatively weak intermolecular interactions. As opposed to the PL QY behaviors of compounds **1-3**, compound **4** bearing bulky carbazolyl end-groups exhibited negligible dependence of the QY on the water fraction in the mixture, and retained the QY value (34%) in aggregates similar to that estimated in dilute solution or PS matrix. The spatial restrictions occurring in the aggregated phase had no effect on the PL efficiency, since fast intramolecular motions were already suppressed by the bulky carbazolyl moieties.

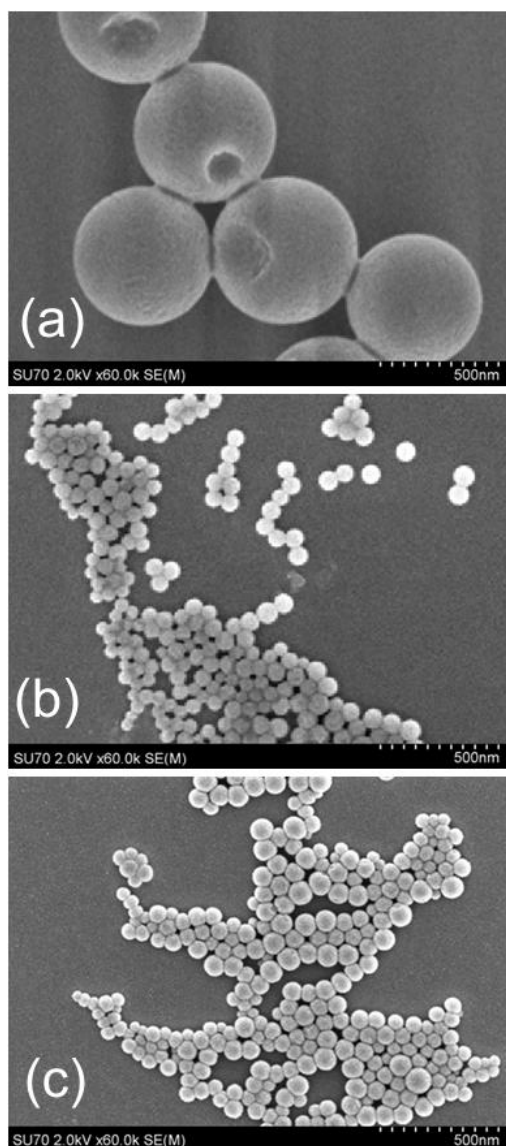


Fig. 4.5. SEM images of the compound **2** nano-aggregates formed in THF/water mixtures with 70 (a), 80 (b), and 90 (c) volume percent of water.

Scanning electron microscopy aided in visualizing the pyrrolo [2,3-d]pyrimidine-based molecular aggregates casted on crystalline silicon substrates. The typical SEM images of the compound **2** nanoaggregates formed in THF/water mixtures with 70, 80, and 90 volume percent of water are displayed in Fig. 4.5. The similar images were also acquired for the rest of the compounds revealing an almost perfectly round shape of their aggregates formed at the different THF/water ratio, and thus verifying their amorphous nature [52]. A clear tendency of the reduction of mean particle size with the increasing water fraction was observed. The mean diameters of the nanoaggregates of all the pyrrolo[2,3-d]pyrimidine compounds varied from about 600 nm (at 70% of water) to less than 50 nm (at 90% of water).

Fluorescence microscopy was employed for imaging the large ensembles of pyrrolo[2,3-d]pyrimidine nano-aggregates formed in THF/water (1/9) mixtures and casted on glass

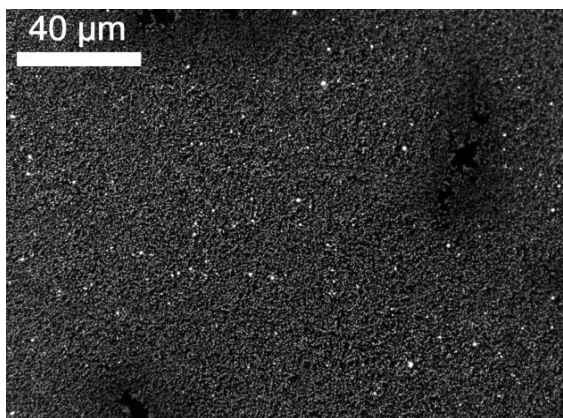


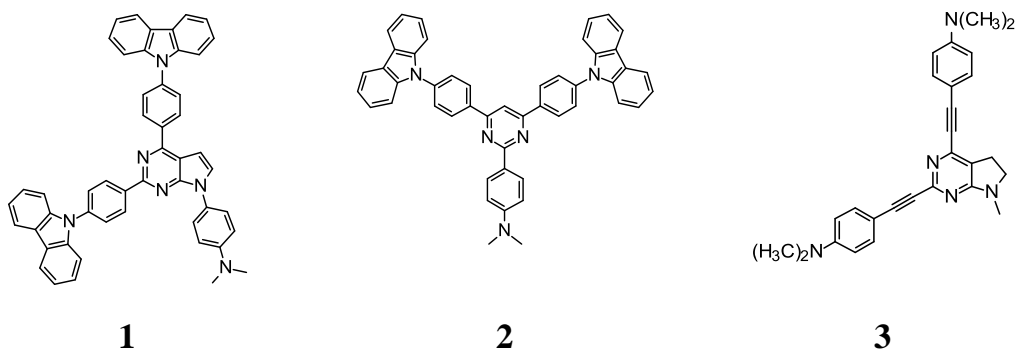
Fig. 4.6. Fluorescence microscopy image of the compound **2** fluorescent nanoaggregates formed in THF/water (1/9) mixture.

substrates. Fig. 4.4 shows the fluorescence microscopy image of compound **3** fluorescent nanoparticles, which were easily discerned against the 'dark' background owing to their high PL efficiency. The compounds **2**, **4** and **5** demonstrated similar homogeneously distributed and well separated fluorescent nanoaggregates formed at the water fraction of 90% in the water/THF mixtures.

In summary, water-stable FONs from sterically-hindered pyrrolo[2,3-d]pyrimidine compounds have been successfully formed by the reprecipitation technique. The aggregation induced emission with a maximal 20-fold emission efficiency enhancement (from 1% up to 20%) was obtained. The size tuning of the FONs in the range of 50-600 nm can be accomplished by controlling solvent/non-solvent ratio in the THF/water mixtures. Spherical shape of the FONs revealed by SEM accompanied by featureless PL bands indicates the dominant amorphous nature of the nanoparticles.

4.2 Pyrimidine and pyrrolo[2,3-d]pyrimidine derivatives for fluorescent metal ion sensing

Due to the distinct sensitivity to the effects of surrounding media, molecular donor-acceptor systems are widely researched for fluorescent metal ion sensing applications [53]. Usually such systems are comprised of a fluorophore (in our case pyrimidine or pyrrolo[2,3-d]pyrimidine compounds) and a receptor, where the metal ion binds. This chapter analyses the influence of several metal ions to the fluorescence properties of pyrimidine and pyrrolo[2,3-d]pyrimidine compounds with donor-like dimethylamine moieties. Dimethylamine units are one of the strongest electron-donors and their incorporation into the molecular donor-acceptor systems leads to the most prominent changes of fluorescence properties upon the variation of environment [19], [53]. The structures of the selected compounds are presented in figure 4.7.



4.7 pav. Molecular structures of the selected derivatives.

Absorbance and fluorescence spectra of the dilute solutions of the fluorophores with the presence of different concentrations of various metal ions (Ag, Cd, Cu, Co, Ni, Pb and Zn) have been determined. Usually the introduction of metal ions results in severe quenching of the fluorescence. Only in some systems fluorescence enhancement is observed and is often related to prominent changes in the charge transfer between donor and acceptor moieties of the molecule and is effected by their intramolecular twisting (TICT) [19]. Selected pyrimidine and pyrrolo[2,3-d]pyrimidine derivatives with dimethylamine moieties demonstrated selectivity of their optical properties to Hg^{2+} and Fe^{2+} ions, which manifested in three different effects - fluorescence enhancement, fluorescence spectra shifting and absorbance spectra shifting accompanied by fluorescence quenching.

Compounds bearing dimethylamine fragments usually exhibit dual fluorescence as a result of twisting induced charge transfer (TICT) reactions. The fluorescence of planar configuration of the molecules manifests in the fluorescence bands of higher energy, while the red-shifted bands are attributed to the charge transfer states of the twisted molecular conformations. The presence of metal ions inhibits the twisting of the molecules, thus the intensity of the locally excited (LE) fluorescence band is enhanced.

The addition of Hg^{2+} ions resulted in a dramatic increase of the LE fluorescence band up to 190 times of the THF solution of compound **1**. The most efficient fluorescence enhancement occurs when one molecule of **2a** binds with 4 Hg^{2+} ions. Similar but less prominent enhancement of the LE fluorescence band (up to 65 times) was observed for Fe^{2+} ions. The fluorescence of the THF solution of compound **2** without any metals shows the TICT fluorescence band at 575 nm, while the addition of

the Hg^{2+} ions results in its reduced intensity and the emergence of the LE fluorescence band at 454 nm. The presence of Hg^{2+} ions led to dramatic changes in the absorption spectra of compound **3**, accompanied by prominent fluorescence quenching. Most likely in this case stable molecular complexes are formed already in the ground state. Pictures of the fluorescence and absorbance changes of compounds **2** and **3** are shown in figure 4.8.

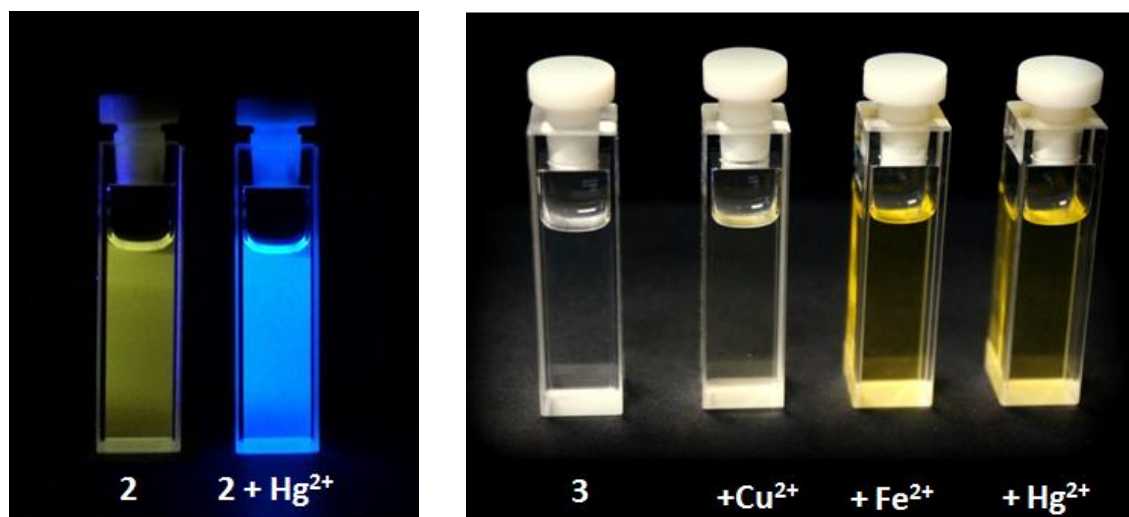


Fig. 4.8. Fluorescence and absorbance changes of compounds **2** and **3**.

In conclusion, Pyrimidine and pyrrolo[2,3-d]pyrimidine compounds exhibit fluorescence sensing properties, induced by the TICT reactions, which are prone to the presence of Hg^{2+} and Fe^{2+} ions. This enables selective detection of Hg^{2+} and Fe^{2+} against ions of other metals (Ag, Cd, Cu, Co, Ni, Pb, Zn). The presence of the Hg^{2+} ions resulted in the fluorescence enhancement up to 190 times. Pyrrolo[2,3-d]pyrimidine derivative with two dimethylamine moieties exhibited the formation of metal complexes already in the ground state.

List of author's publications

Scientific articles

1. S. Tumkevicius, J. Dodonova, K. Kazlauskas, V. Masevicius, L. Skardziute, S. Jursenas, „Synthesis and photophysical properties of oligoarylenes with a pyrrolo[2,3-d]pyrimidine core“, *Tetrahedron Letters* **51**, 3902-3906 (2010).
2. J. Dodonova, L. Skardziute, K. Kazlauskas, S. Jursenas, S. Tumkevicius, „Synthesis of 4-aryl-, 2,4-diaryl- and 2,4,7-triarylpyrrolo[2,3-d]pyrimidines by a combination of the Suzuki cross-coupling and N-arylation reactions“, *Tetrahedron* **68**, 329-339 (2012).
3. A. Kovaļovs, I. Novosjolova, Ē. Bizdēna, I. Bižāne, L. Skardziute, K. Kazlauskas, S. Jursenas, M. Turks, "1,2,3-Triazoles as leaving groups in purine chemistry: a three-step synthesis of N6-substituted-2-triazolyl-adenine nucleosides and photophysical properties thereof", *Tetrahedron Letters* **54**, 850–853 (2013).
4. L. Skardziute, K. Kazlauskas, J. Dodonova, J. Bucevicius, S. Tumkevicius, S. Jursenas, “Optical study of the formation of pyrrolo[2,3-d]pyrimidine-based fluorescent nanoaggregates”, *Tetrahedron* **69**, 9566-9572 (2013).
5. L. Skardziute, J. Dodonova, A. Voitechovicius, J. Jovaisaite, R. Komskis, A. Voitechoviciute, J. Bucevicius, K. Kazlauskas, S. Jursenas, S. Tumkevicius. "Synthesis and optical properties of the isomeric pyrimidine and carbazole derivatives: Effects of polar substituents and linking topology" *Dyes and Pigments* **118**, 118-128 (2015).
6. J. Bucevicius, L. Skardziute, J. Dodonova, K. Kazlauskas, G. Bagdziunas, S. Jursenas, S. Tumkevicius. "2, 4-Bis (4-aryl-1, 2, 3-triazol-1-yl) pyrrolo [2, 3-d] pyrimidines: synthesis and tuning of optical properties by polar substituents." *RSC Advances* **5**, no. 48, 38610-38622 (2015).

Conference presentations presented by author

1. "Multifunctional iridium-based metal-ligand complexes for phosphorescent OLED's", L. Skardžiūtė, K. Kazlauskas, S. Juršenas, D. Tomkutė-Lukšienė, T. Malinauskas, V. Getautis, 38th Lithuanian National Conference of Physics, Vilnius, June 8-10, 2009.

2. *"Phosphorescence of multifunctional iridium-based metal-ligand complexes"*. L. Skardžiūtė, K. Kazlauskas, S. Juršėnas, D. Tomkutė-Lukšienė, T. Malinauskas, V. Getautis, *Advanced Materials And Technologies*, August 27-31 2009, Palanga
3. *"Triplet emitting complexes with charge transporting units"*, L. Skardžiūtė, K. Kazlauskas, S. Juršėnas, D. Tomkutė-Lukšienė, T. Malinauskas, V. Getautis, 53rd Scientific student conference of physics "Open readings", March 24-27 2010, Vilnius
4. *"Funkcinių arilo grupių įtaka pirol[2,3-d]pirimidino junginių fluorescencinėms savybėms"*, L. Skardžiūtė, K. Kazlauskas, S. Juršėnas, J. Dodonova, S. Tumkevičius, First conference of young scientists „*Fizinių ir technologijos mokslų tarpdalykiniai tyrimai*“, February 8 2011, Lithuanian academy of sciences, Vilnius
5. *"Influence of Polar Groups on Photophysical Properties of Oligoarylenes with a Pyrrolo[2,3-d]pyrimidine Core"*, L. Skardžiūtė, K. Kazlauskas, A. Gruodis, J. Dodonova, S. Tumkevičius, S. Juršėnas, 4th International Symposium on Flexible Organic Electronics, July 11-13 2011, Thessaloniki, Greece
6. *„Impact of functional Substituents on Photophysical Properties of Pyrrolo[2,3-d]pyrimidine Compounds“*, L. Skardžiūtė, K. Kazlauskas, S. Juršėnas, J. Dodonova, S. Tumkevičius. *„Electronic and Related Properties of Organic Systems“*, July 11-13 2011, Vilnius.
7. *„Tailoring of Photophysical Properties of Pyrrolo[2,3-d]pyrimidine Compounds“*, L. Skardžiūtė, K. Kazlauskas, S. Juršėnas, J. Dodonova, S. Tumkevičius. *„Advanced Materials and Technologies 2011“*, August 27-31 2011, Palanga.
8. *„Pirolo[2,3-d]pirimidino fotofizikinių savybių valdymas poliniais pakaitais“*, L. Skardžiūtė, K. Kazlauskas, S. Juršėnas, J. Dodonova, S. Tumkevičius. *„Lithuanian National Conference of Physics“*, October 08-11 2011d., Vilnius
9. *"Impact of polar substituents on the photophysical properties of the pyrrolo[2,3-d]pyrimidine derivatives"*, L. Skardžiūtė, K. Kazlauskas, A. Gruodis, J. Dodonova, S. Tumkevičius, S. Juršėnas. *"Vth International Conference on Molecular Materials. MOLMAT"*, 3 - 6 July 2012, Barcelona.

10. "Effect of conformation and polarity changes on the photophysical properties of pyrrolo[2,3-d]pyrimidine compounds", L. Skardžiūtė, K. Kazlauskas, A. Gruodis, J. Dodonova, S. Tumkevičius, S. Juršėnas. "International Conference on Optical Probes of Conjugated Polymers and Organic Nanostructures", July 14-19 2013, Durham.
11. "Pyrrolo[2,3-d]pyrimidine derivatives as potential fluorescent sensors", L. Skardziute, J. Jovaisaite, A.Gruodis, K. Kazlauskas, J. Dodonova, S. Tumkevicius, S. Jursenas. XVth International Krutyn Summer School "Challenges to open up the new era of organic photonics and electronics from material to market – from Asian perspective", Krutyn, Masurian Lake district, Poland, June 8 -14, 2014.
12. "Impact of polar substituents on the photophysical properties of novel pyrimidine based compounds", Lina Skardžiūtė, Justina Jovaišaitė, Jonas Bucevičius, Jelena Dodonova, Sigitas Tumkevičius, Saulius Juršėnas, *Electronic Processes in Organic Materials*, May 04-09 2014, Lucca (Barga) Italy .

Conference presentations presented by co-authors

1. "2,4-Diarylpyrrolo[2,3-d]pyrimidines: synthesis and photophysical properties", J.Dodonova, L.Skardžiūtė, K.Kazlauskas, S.Juršėnas, S.Tumkevičius, 9th Lithuanian conference of chemistry "Chemija 2009", October 14th 2009, Vilnius.
2. „Synthesis and properties of ditriazolylpurine nucleosides“, I. Novosjolova, A. Kovalovs, I. Bizane, L. Skardziute, K. Kazlauskas, S.Jursenas, E. Bizdena, M. Turks, "Organic chemistry", April 25 2012, Kaunas..
3. „Pyrrolo[2,3-d]pyrimidine derivatives as fluorescent agents“, L. Skardziute, J. Jovaisaite, A. Gruodis, K. Kazlauskas, J. Dodonova, S. Tumkevicius, And S. Juršėnas, International materials research congress IMRC XXIII, General program, 17-21 August, 2014, Cancun, Mexico.

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