VILNIUS UNIVERSITY
CENTER FOR PHYSICAL SCIENCES AND TECHNOLOGY

STEPAS TOLIAUTAS

ELECTRONIC EXCITATION PROCESSES OF PHOTOACTIVE ORGANIC MOLECULES

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STEPAS TOLIAUTAS

ELEKTRONINIO SUŽADINIMO PROCESAI FOTOAKTYVIOSE ORGANINĖSE MOLEKULĖSE

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1. Introduction

1.1. Electronic excitation processes

Photoactive, or *light-sensitive* molecules are found in most living organisms. For example, plants and some bacteria employ such molecules in the process of photosynthesis, that is, conversion of light energy to chemical energy. Many animals also have visual sensors that extract information about their surroundings from the collected light, and photoactive molecules form the basis of these visual sensors. Such molecules are known as *pigments* (light-sensitive parts of the protein), *chromophores* (molecules that determine the color of the material) or *photochromes* (materials that change their color upon light-excitation) in the literature. The interaction of the molecule with the photon (quantum of light) results in the change of the molecular energy. Since the energy delivered by visible light induces changes in the electronic subsystem of the molecule first, this type of interaction is called the ***electronic excitation***. To distinguish the interaction with visible light, the term "*optical excitation*" is sometimes used as well.

Electronic excitation of the molecule usually signals the start of one of the various energy-related ***processes*** within the molecule. Such process may be irreversible; for example, the provided energy might break the molecule into several parts or enable the chemical reaction with the surrounding material, resulting in the *reaction products*. On the other hand, excited molecule might be able to dissipate the excess energy through the different conversion channels and return to the ground state, resulting in either the initial compounds or the *isomers* of slightly different geometric structure. The repeated process of the excitation and the energy dissipation or *relaxation* constitutes the excitation cycle. Excitation cycles are observed during many physical, chemical and biological phenomena. In many biological systems, such as the proteins within plants and bacteria, photon absorption induces a chain of non-radiative interactions known as the *photocycle* [1,2]. Such proteins are the main elements of the above-mentioned light sensors and energy-harvesting units. The other example of the light-induced reversible reaction is the *optomechanical cycle* – the structural alteration of the molecule or its fragment that can be used to carry out mechanical work [3,4]. Such compounds are expected to be used in the construction of molecular-scale devices and the miniaturization of existing technology. Other relaxation processes are not cyclic; for example, the working principle of the *organic optoelectronics* devices – solar elements and OLEDs – is the light-to-electrical energy conversion [5]. In case of OLED, charge carriers are transported into the photoactive material, which is then used to emit photons. It is clear from the provided examples that the investigation of the electronic excitation processes is very relevant for the research of both the natural organisms and the novel artificial systems.

The main difficulty of theoretical modeling of the electronic excitation processes in molecules is solving the time-dependent Schrodinger equation, which is currently computationally too expensive for systems of practical importance. Direct computations are restricted to small molecules or generalized systems described by a few energy levels and couplings. However, it is possible to circumvent this problem by gradually changing structural parameters of the system and repeatedly solving time-independent Schrodinger equation. Since each set of structural parameters corresponds in principle to a dynamic state at a certain point in time (although not necessarily reachable by the process under investigation), the ***potential energy surfaces (PES)*** obtained this way qualitatively describe the behavior of the excited molecular system and can be used to explain, f. e., the time-dependent spectra without directly solving the dynamic equations.

The widely used group of molecular investigation methods comprises the computational methods of *electronic structure*, based on the molecular theory. The review of the theoretical methods can be found in Chapter 2 of the dissertation. The optimized algorithms of the electronic structure methods are gathered into program packages and made available for the wide circle of scientists – physicists, chemists and biologists, experimentalists and theoreticians alike. Most popular packages include *Gaussian* [6], *GAMESS-US* [7,8], *NWChem* [9]. Together with the implementations of electronic structure methods such packages usually contain structure optimization algorithms, molecular mechanics and molecular dynamics methods, calculation routines of thermodynamic parameters etc. The area of computational molecular science covered by the above-mentioned methods is sometimes called *computational chemistry*, and the quantum-mechanical subset of the theories is known as *quantum chemistry*. Combined use of stationary electronic structure methods and molecular structure optimization algorithms enables researchers to model electronic excitation processes by studying molecular ground- and excited-state potential energy surfaces. The main parameters of the potential energy surfaces of the molecular system are described in Chapter 3 of the dissertation. The PES-based models are constructed and used to describe the processes occurring in the investigated molecular compounds. Dissertation chapters 4–7 contain the descriptions of the studies of four photoactive compounds and the constructed theoretical models. The conclusions that validate the defense propositions are formulated in Chapter 8. The last Chapter lists the scientific articles and conferences where the results of these studies were presented.

1.2. Main goal of the dissertation

The main **goal** of this dissertation is to study processes caused by the electronic excitation in photoactive organic molecules using computational electronic structure methods and to create models based on the potential energy surfaces that describe the energy relaxation in the investigated molecules. The constructed models are then used to solve the following **problems**:

1. To investigate the possible proton transfer pathway in the excited 2-(N-methyl-α-iminoethyl)-phenol (MIEP) and to determine the effect of the polar solvent (water) for the energy relaxation of MIEP.
2. To model the structural changes in the excited indolo-benzoxazine (IB) compound after the opening of the oxazine ring and to characterize the effect of such changes on its photochromic properties.
3. To explain the cause of the efficient phosphorescence in poly[biphenyl(methyl)-silylene] (PBMSi) polymer.
4. To determine the character of the absorption and the phosphorescence in bis(2-phenylbenzothiazole)-iridium-acetylacetonate ($(\mathrm{pbt})_2\mathrm{Ir(acac)}$) and to estimate the effect of carbazole groups on the optical properties of the investigated complex.

1.3. Novelty and importance of the studies

- This work features four new potential energy surface models for the description of the energy relaxation in various photoactive organic compounds.
- Study of the MIEP molecule reveals the properties of the Schiff base – a functional group in the photoactive center of the bacteriorhodopsin protein, performing trans-membrane proton transfer – in the polar environment.
- The PES model of the IB compound explains observed processes of the different timescales within the photochromic molecule that, due to its fatigue resistance, is proposed to be used for molecular-scale switches.
- The model of the phosphorescence in PBMSi polymer provides evidence of the newly-observed physical phenomenon – enhanced intersystem crossing in the conjugated polymer without involving heavy-metal effect. Such materials are promising for non-coherent up-conversion and white-light OLED applications.
- The $(pbt)_2Ir(acac)$ complex model reveals the structural properties of the complex and its interaction with additional functional groups.

1.4. Propositions for the defense

- The energy relaxation process of the excited MIEP molecule in water is governed by the formation of the hydrogen-bonded molecular complex consisting of the MIEP and the solvent molecules adjacent to the Schiff base of the compound.
- Photochromic properties of the excited IB compound are determined by several relaxation pathways that are related to the movement of the nitrophenol group after the opening of the oxazine ring.
- The efficient phosphorescence of the PBMSi polymer is caused by the presence of charge-transfer state between the electronic systems of the silicon chain and biphenyl groups of the material.
- The excitation of the $(pbt)_2Ir(acac)$ complex has only small effect on its structure and is not affected by the addition of the functional carbazole groups.

2. Parameters of the potential energy surfaces

2.1. Jablonski diagrams and the potential energy surfaces

Energy conversion processes in chemistry and chemical physics are commonly depicted as Jablonski diagrams [10]. Nowadays, the Jablonski diagram is understood as a broad tool, assuming different forms for the different uses [11]. However, the transitions between states with the different molecular structure are decidedly vague in Jablonski diagrams. By including the information about the reaction coordinate or coordinates in the *x* axis, Jablonski diagram becomes the potential energy curve or surface diagram (Fig. 2.1) which may have many special points on it – transition/ saddle points, excited-state minima, intersection points etc.

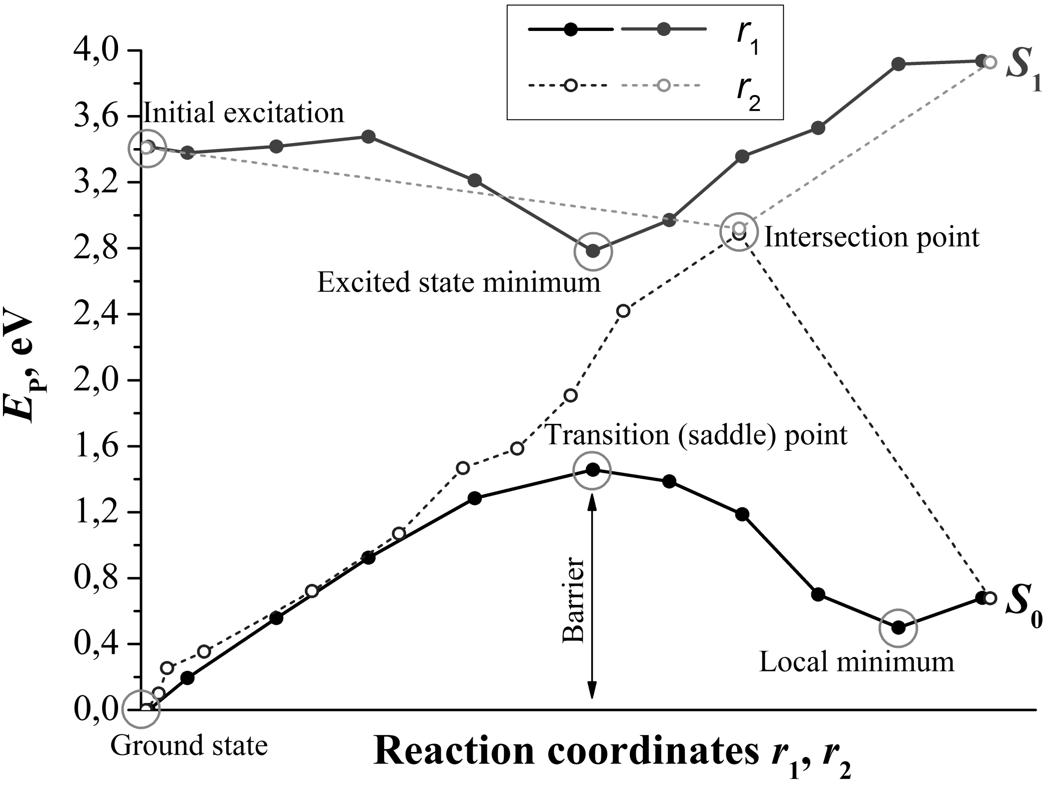

Figure 2.1. *Potential energy curves of the photoactive molecule*

2.2. Main parameters of the potential energy surfaces

The main calculated parameters of the potential energy surfaces of the photoactive molecules are:

- ***Ground-state energy*** or molecular bonding energy (needed to break-up the molecule into the non-interacting nuclei and electrons). The ground-state energy is the main variational parameter of both *ab initio* (post-Hartree-Fock) [12] and density functional [13] methods, so it is the principal quantity obtained by the electronic structure calculations. Since the ground-state energy of the various conformers of the photoactive molecules might (and is expected to) differ, the *potential energy* (with respect to some chosen point, such as optimized ground state structure) is used for the characterization of the time-dependent processes.
- ***Excitation*** or ***excited-state energies*** of low-lying states that are usually involved during the photoexcitation process. The excited-state energies are usually calculated using correlation-corrected *ab initio* methods based on perturbation theory [14], configuration interaction [15], multiconfigurational wavefunctions [16] or the time-dependent density functional theory [17].
- Properties and special points of the ***potential energy surfaces*** are found by performing structure optimizations and transition state searches in the ground and excited states. Intersection points between states can also be found using several new methods [18,19].
- Intensity of the electronic transition is commonly estimated using ***oscillator strength*** which is related to the quantum-mechanical transition dipole moment of the particular excitation [20]. It may be calculated either directly from the transition moments or indirectly (which is the case of the TD-DFT).
- Electronic distribution can be visualized quantitatively – as changes in ***electron density*** – or through the qualitative properties of the ***molecular orbitals*** that represent individual electrons. Molecular orbitals may offer better connection to the chemical description of the studied process, but in most systems the single-orbital, single-excitation model is insufficient and has to be used with caution.

3. Solvent effect on the proton-transfer processes in MIEP

Light-induced proton transfer is an important part of the processes in biological systems. Since such processes are very sensitive to the effects of the environment [21], the proton transfer may be enabled [22], enhanced or suppressed [23], depending on the surroundings of the photoactive complex. For example, proton transfer in the active center of the bacteriorhodopsin protein is caused by the light absorption in the retinal chromophore, which triggers movement of the attached Schiff base (Fig. 3.1) [24]. The active center is also known to contain several "trapped" water molecules, effect of which for the proton transfer is not entirely clear [25].

Various factors that may influence the processes in the active center of bacteriorhodopsin and the relative importance of said factors are investigated by studying various structural groups of the active center (e. g. Schiff base), both together with their surroundings and as separate model compounds [26]. The unit of phenol ring and Schiff base, which share the proton between them, forms the basis of the aromatic anil group of molecules that exhibit many interesting properties, such as intramolecular proton transfer [27] and related photochromism [28]. Experiments on one such compound, N-(triphenylmethyl)-salicydenimine (MS1) in ethanol, showed that the energy relaxation of the excited compound is strongly influenced by the solvent molecules [29]. The solvent effect on the properties of 2-(N-methyl-α-iminoethyl)-phenol (MIEP) in the electronic ground state was also modeled earlier [30]. The main task of the current study was to investigate possible proton transfer pathway in excited MIEP molecule in water and to determine the (polar) solvent effect for the energy relaxation of the compound.

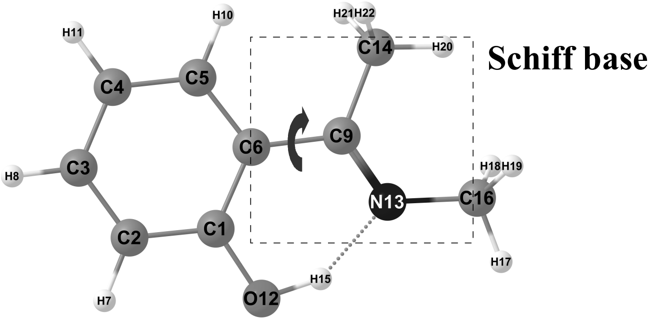

Figure 3.1. *Molecular structure of MIEP in vacuum*

3.1. Structural model and computational methods

Molecular structure of the MIEP compound in the ground state S_0 (in vacuum) is shown in Fig. 3.1. The study reveals that both the inclusion of the polar solvent and the electronic excitation of the molecule result in the shift of the proton H_{15} to the nitrogen atom N_{13}. During the excitation the molecule undergoes additional deformation by the twisting of C_6-C_9 bond, which leads to the further proton transfer. The solvent effect on the electronic states of the MIEP compound during the proton transfer is modeled here in several ways: through the polarizable continuum model, by forming a shell of water molecules around the compound and by directly calculating the properties of the molecular complex of MIEP and water molecules nearest to its Schiff base.

Time-dependent density-functional theory (TD-DFT) employing B3LYP functional and cc-pVTZ basis set was used for most of the calculations, performed by *Gaussian09* [6]. Conical intersection between ground and first excited electronic state, which is commonly used to explain relaxation properties for this class of molecules, was found by the algorithm [19] implemented in *GAMESS-US* [8]. For the solvent effect, conductor-like model (C-PCM) [31] and several types of two-level ONIOM model [32] were used.

3.2. Deformation pathway of MIEP in vacuum

As noted in the previous section, ground state of the MIEP molecule in vacuum corresponds to the **enol** tautomer, which has proton connected to the oxygen atom of the phenol group. After the excitation, the proton moves towards the nitrogen atom of the Schiff base and the ***cis*-keto** tautomer is formed. The evolution of the first excited state also leads to the deformation of the molecule from the C_s-symmetric structure via the twisting of the Schiff base around the C_6-C_9 bond. The potential energy curves corresponding to the change of the **twisting angle d_{CCCN}** are presented in Fig. 3.2. At the end of the range of the twisting motion the local ground-state energy minimum, corresponding to the slightly asymmetric *trans*-keto tautomer, is found. Excited-state energy S_1

minimum and conical intersection point between S_0-S_1 states are located in the middle of the motion range, albeit with the slight changes in the structure of the Schiff base. The excited-state minimum and conical intersection point share many similarities in their wavefunction character, which indicates that the MIEP molecule is likely to have two competing energy relaxation pathways, manifesting as fluorescence from the excited state and the non-radiative relaxation through the intersection point.

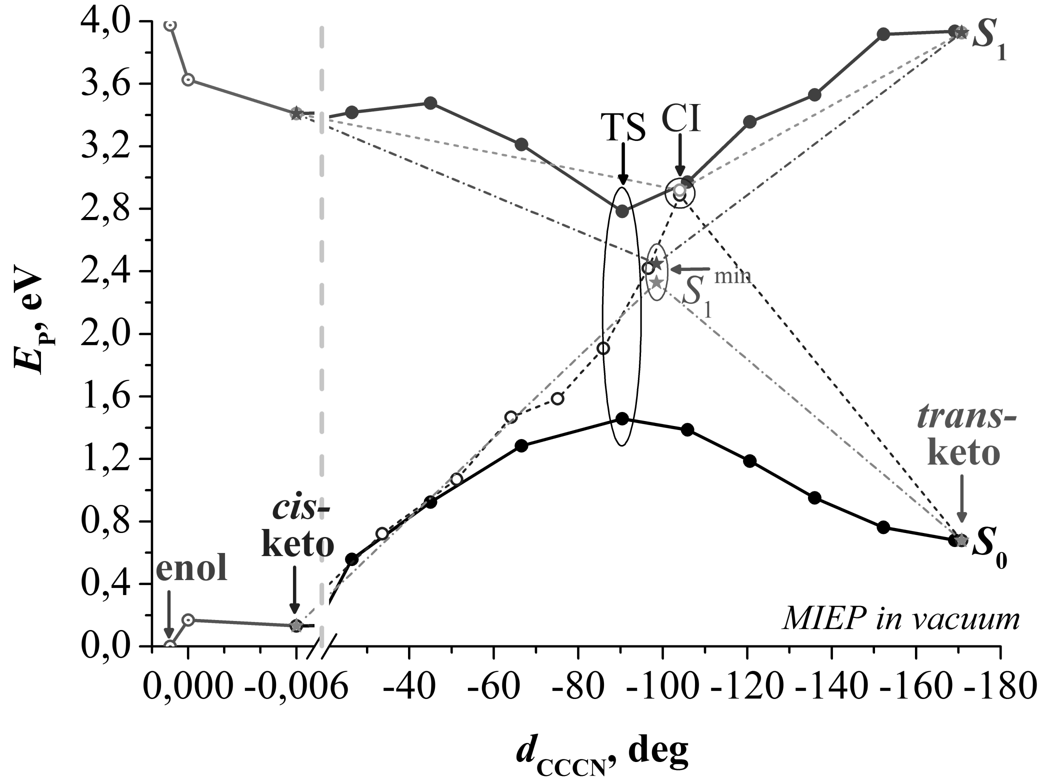

Figure 3.2. *Potential energy curves of MIEP in vacuum*

3.3. Changes of MIEP properties in solvent

Inclusion of the continuum solvent model brings the first change to the excitation properties of MIEP, namely, that the most stable conformation in the ground state S_0 now corresponds to the *cis*-keto tautomer. This is in line with the earlier study [30]. On the other hand, the potential energy curves retain their shape. To examine whether these properties are also retained after direct inclusion of the solvent effects on the fairly small molecule, the calculations of the MIEP in the solvent shell were performed. It was noticed that several molecules nearest to the Schiff base of the compound form strong (less than 2 Å) hydrogen bonds with MIEP (Fig. 3.3a), while all other solvent molecules remain more distant (more than 2.5 Å). Due to this finding it was decided to perform direct calculations of the electronic properties of the molecular complex of MIEP and four water molecules (Fig. 3.3b).

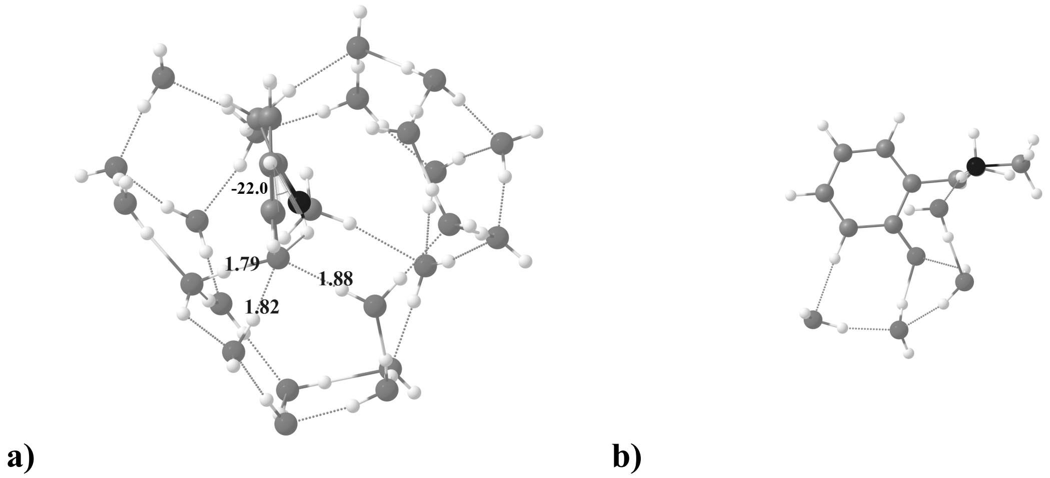

Figure 3.3. *MIEP molecule in water shell (a) and as a supramolecular complex (b)*

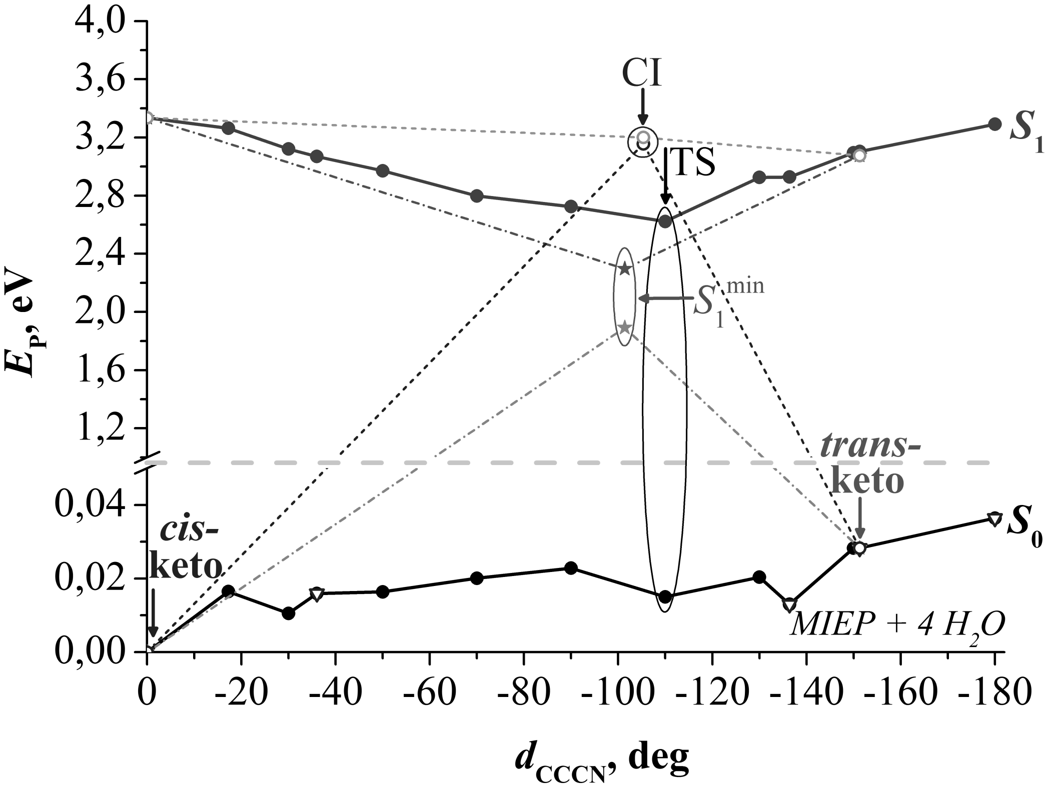

Figure 3.4. *Potential energy curves of MIEP-4H_2O complex*

Resulting potential energy surfaces are presented in Fig. 3.4. It is clear that the inclusion of nearby water molecules considerably changes the shape of the ground-state energy surface; instead of the single saddle point, it is now almost completely flat, with several shallow minima. Moreover, the *trans*-keto tautomer does not belong to the one of the minima as it did before. Excited-state energy surfaces are not affected as much, although the conical intersection point is now somewhat higher than the excited-state minimum, hinting at the possible strengthening of the radiative emission channel.

3.4. Comparison to MS1

The experimental studies of the photochromism of MIEP have not been performed as of yet. However, the identified properties of the compound are in very good agreement with the findings of the investigation of similar MS1 compound in another polar solvent (ethanol). The excitation of MS1 generates intermediate structures and long-living photoproducts shifted by 30 nm to the lower energies. The excited-state pathways and the flat ground-state surface of MIEP would result in a similar observed behavior. Additionally, neither MIEP in water nor MS1 in ethanol exhibit the photoproduct corresponding to the *trans*-keto tautomer. Therefore, the observed relaxation properties of the excited aromatic anil molecules are most probably caused by the direct interaction of the compounds with the polar solvent molecules via the hydrogen-bonding.

▼▼▼

4. Photochromic properties of indolo-benzoxazine

The change of the optical properties of photochromic materials after excitation is usually linked to the reversible structural deformation of the molecules [3]. Since such deformation may include the spatial movement of the chemically active group or the formation of controlled intermediate structure, the photochromic molecules are proposed to be used as molecular-scale building blocks, for example, in high-density data storage

[33]. Among such molecules, spiropyrans [34] and coumarins [35] are known for their excellent resistance during many excitation cycles. 5a,6-dihydro-12h-indolium[2,1-b][1,3]benzoxazine (indolobenzoxazine, IB) is one such compound, which exhibits ultra-fast light-induced ring opening and formation of distinct chromophoric groups [36]. While the experimental results of the compound are tentatively ascribed to the excitation dynamics of the two constituent moieties, 3H-indolium and 4-nitrophenol, the precise dynamics is quite complicated and cannot be easily interpreted. The main task of the theoretical investigation presented in this chapter was to determine the structure of the electronic states of the IB compound and its constituent moieties and model the evolution of the compound after the oxazine ring opening.

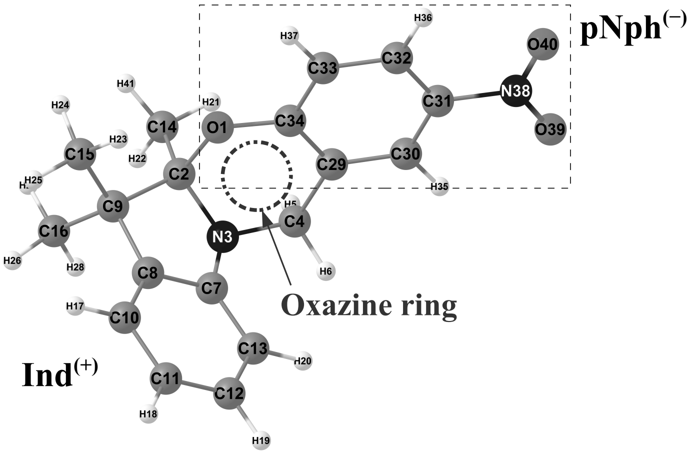

Figure 4.1. *Molecular structure of IB compound*

4.1. Structural model and computational methods

The IB compound in the ground state is shown in Fig. 4.1 together with the markings of the 3H-indolium (Ind) and 4-nitrophenol (pNph) chromophoric groups. The joining site of the chromophoric groups constitutes a deformed oxazine ring. During light excitation the O_1-C_2 bond is cleaved, resulting in the ring opening. Several local energy minima corresponding to the open-ring structures are found during the investigation. To describe the energy relaxation of the excited compound through the local minima, two simplified reaction coordinates are used.

Time-dependent density-functional theory (TD-DFT), as implemented in *Gaussian03* [6] and *GAMESS-US* [8] packages, was used for the calculations. Positions of ground-state energy minima were found using B3LYP functional and 6-311++(2d,p) basis set, while the excited-state spectra for all structures were obtained using LC-BOP functional and cc-pVDZ basis set. Polarizable continuum model [31] was used to include the effects of acetonitrile solvent used in experiments [36].

4.2. Reaction coordinates of IB compound

In addition to the ground-state structure M0, two local energy minima of the IB compound were located. The minima, M1 and M2, correspond to the open-ring form of the compound, obtained by **twisting 4-nitrophenol** group around the N_3-C_4 bond in different directions. Two minima of the first excited state S_1, E1a and E1b, were also located near the ground-state minima. Additionally, the excited-state energy minimum of the S_2 state, E2, was found near the optimal ground-state structure. While the twisting angle of the N_3-C_4 bond qualitatively describes the changes in the 4-nitrophenol group, additional coordinate was needed to indicate the evolution of the **3H-indolium**; out of all oxazine ring-related coordinates (Table 4.1), angle of the N_3 atom to the symmetry plane of 3H-indolium was selected. Ground-state potential energy surface corresponding to the selected reaction coordinates is presented in Fig. 4.2. Ground- and excited-state minima are marked on the resulting surface.

Table 4.1. *Geometric parameters of the oxazine ring within IB complex for the various points on the potential energy surfaces. Values in italic represent the broken chemical bond*

	M1	**E1a**	**T01**	**M0**	**E2**	**T02**	**M2**	**E1b**
$r(O_1$-$C_2)$, Å	*2.943*	*2.780*	*2.436*	1.479	1.509	*2.524*	*3.209*	*3.189*
$d(C_8$-C_7-N_3-$C_4)$, deg	**172.1**	**172.5**	**161.9**	**155.4**	**154.7**	**165.6**	**175.1**	**153.9**
$a(N_3$-C_4-$C_{29})$, deg	111.6	110.5	108.6	111.2	110.6	116.0	113.4	108.8
$d(N_3$-C_4-C_{29}-$C_{34})$, deg	**−61.1**	**−55.8**	**−50.1**	**−17.1**	**−20.2**	**33.5**	**49.2**	**54.1**
$a(C_4$-C_{29}-$C_{34})$, deg	117.8	117.3	118.5	119.0	117.8	120.6	116.9	118.3

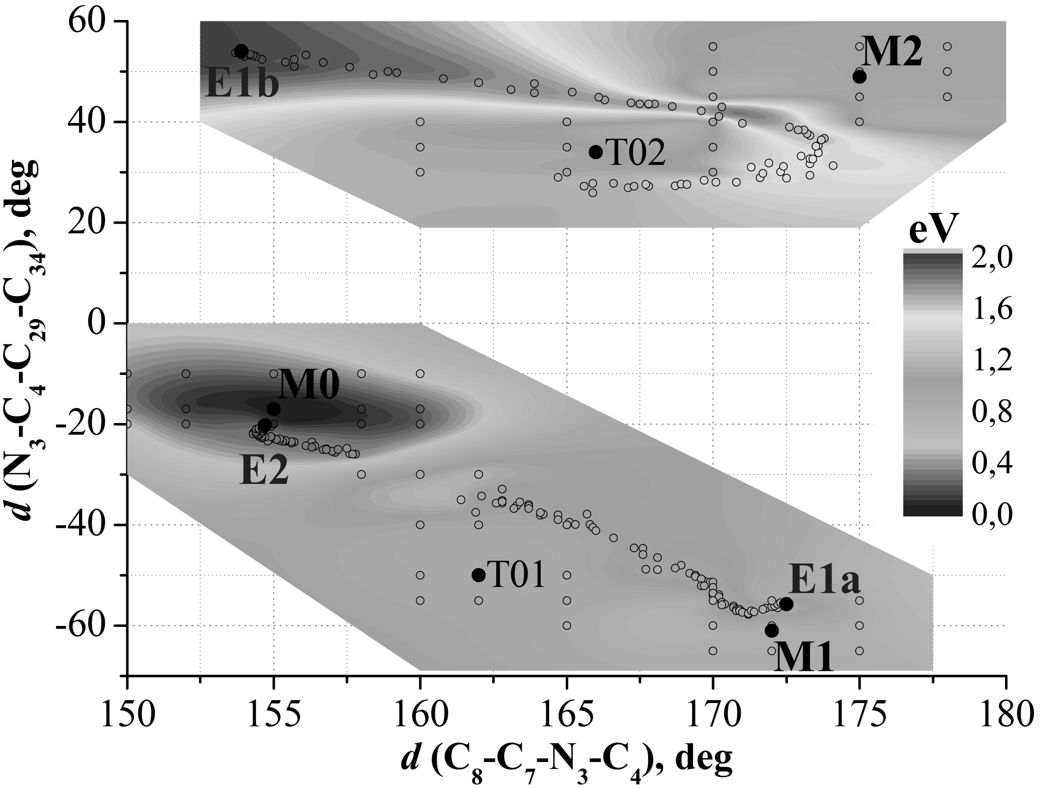

Figure 4.2. *Potential energy surface of the ground state of IB compound*

4.3. Relaxation pathways of the IB compound

The ground- and excited-state potential energy curves, as well as relaxation pathways of the optical excitation, are shown in Fig. 4.3. Comparing calculation results with the spectral measurements of IB compound [36], the following conclusions can be drawn:

- The absorption peak of the IB compound is mainly due to the absorption of the 4-nitrophenol group.
- Cleavage of the O_1-C_2 bond results in the immediate formation of the partially-charged 3H-indolium group. This is confirmed by the calculated partial charges of the chromophoric groups within the compound that are equal to about ±0.5*e* for all open-ring structures.
- The delayed formation of the deprotonated pNphe- group is caused by the conformational changes, namely, the twisting of the 4-nitrophenol group around the N_3-C_4 bond. Additionally, the formation yield is not 100 %, because there is a

relaxation channel through the excited state E2 which does not result in the significant deformation of the compound.

- Long-lasting spectral signals of the IB compound can be explained by the existence of the local ground- and excited-state minima. Ground-state minima M1 and M2 are reached though the excited-state minimum structures E1a and E1b, formed by the interaction between 3H-indolium and 4-nitrophenol groups. IB compound is able to revert from the local minima to the initial state by thermalization due to the shallow potential energy surface and low barriers between different states.

It has to be noted that the recent experimental studies of the derivative IB compound [37] confirm the presence of the open-ring structures formed via the first excited state, as well as the short-lived cleaved-bond state without the significant charge separation.

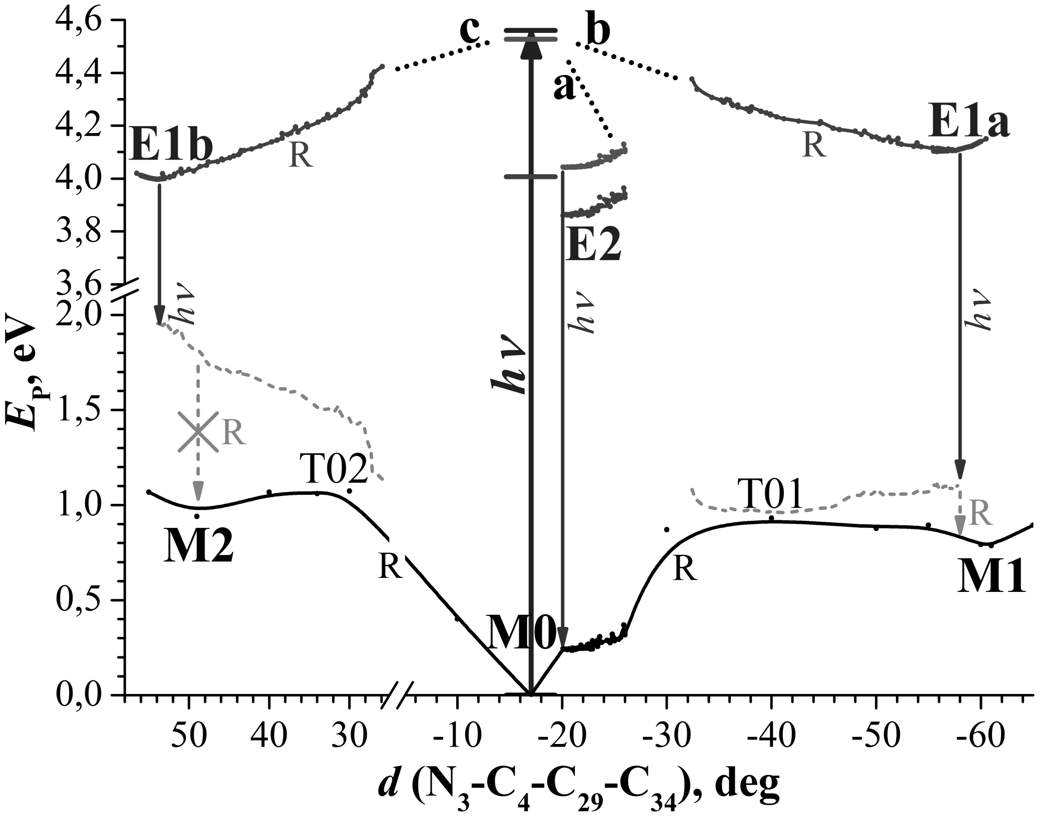

Figure 4.3. *Potential energy curves and relaxation pathways of IB compound*

5. Efficient phosphorescence of PBMSi polymer

Most popular OLED emitter materials used today are almost invariably based on the spin-orbit interaction phenomenon that allows non-radiative conversion between singlet and triplet excited states, as well as emission from the lowest triplet state to the singlet ground state [38]. This is achieved by doping the materials with triplet emitter complexes formed around the heavy-metal atom, such as iridium or platinum [39,40]. The charge-carrier properties of the material can be enhanced by adding functional groups, such as carbazoles [41], to the complexes. The main drawback of the organometallic complexes is the discrepancy in efficiency of red-green emitters and blue-emitting materials [42]. Therefore new materials with higher triplet states and better charge-transfer properties are heavily searched for.

Organic semiconductors without the presence of heavy-metal atoms ordinarily exhibit only extremely weak (in the order of 10^{-4}) phosphorescence. However, experiments on silicon-based PBMSi polymer have established extremely efficient phosphorescence in this polymer, with quantum yield of up to 15 %. The emission is believed to originate from the biphenyl side-groups, even when only the Si chain is excited. The main task of the following study was to determine the electronic state structure of the PBMSi-comparable model compound and explain the cause of the observed emission of the polymer.

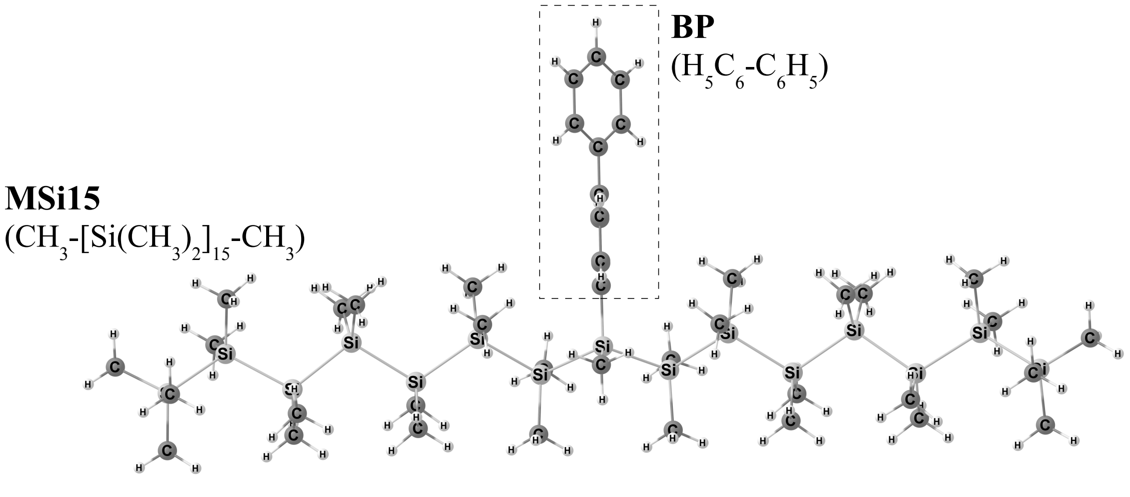

Figure 5.1. *Molecular structure of MSi15-BP compound*

5.1. Structural model and computational methods

Due to the obvious difficulties of calculating the properties of 40- to 50-element long polymer with side-groups, PBMSi was modeled by joining methylated Si-chain and the single biphenyl group in the center of the chain. The structure of the resulting compound, MSi15-BP, is shown in Fig. 5.1.

Time-dependent density-functional theory (TD-DFT) employing B3LYP functional and the 6-31G(d,p) basis set was used for the most calculations performed by the *Gaussian09* package [6]. Additional *GAMESS-US* [8] calculations by the GMC-QDPT method [43] were performed for the validation of the TD-DFT wavefunction character.

5.2. Charge-transfer state of MSi15-BP

Calculated parameters of the excited electronic states of MSi15-BP compound are summarized in Table 5.1. According to both TD-DFT and GMC-QDPT calculations, the lowest excited singlet state S_1 is of a **charge-transfer** character, corresponding to the charge redistribution from the Si chain onto the biphenyl group (Figure 5.2, 1-1'). Second singlet excited state S_2 corresponds to the Si chain excitation, while the absorption of the biphenyl group is located significantly higher. Lowest (emitting) triplet state of the compound T_1 shows the character of the **biphenyl** group.

Table 5.1. *Calculated parameters of the excited electronic states of MSi15-BP compound*

TD-DFT					*GMC-QDPT*				
No.	**E_t, eV**	**f_{osc}**	**Transition**		**No.**	**E_t, eV**	**f_{osc}**	**Transition**	
T_1	3.169	-	3-1'	BP (π-π*)	T_1	3.235	-	2-1'	BP (π-π*)
T_2	3.726	-	1-2'	Si (σ-σ*)	T_2	4.456	-	1-2'	Si (σ-σ*)
T_3	3.815	-	1-1'	CT	**S_1**	**4.836**	**0.405**	**1-1'**	**CT**
S_1	**3.930**	**0.113**	**1-1'**	**CT**	**S_2**	**5.530**	**1.568**	**1-2'**	**Si (σ-σ*)**
T_4	4.019	-	1-1'	CT	T_3	5.687	-	1-3'	CT
S_2	**4.063**	**2.510**	**1-2'**	**Si (σ-σ*)**	T_4	5.925	-	1-3'	CT
S_6	**4.684**	**0.281**	**3-1'**	**BP (π-π*)**	**S_4**	**6.424**	**0.434**	**2-1'**	**BP (π-π*)**

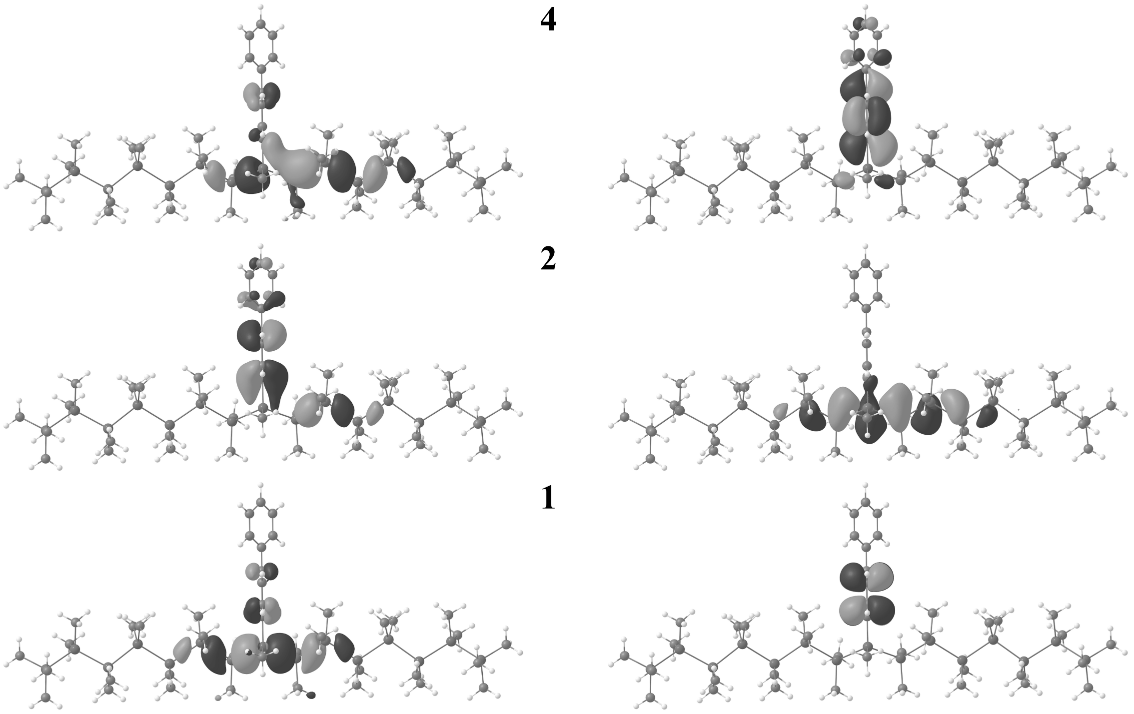

Figure 5.2. *Frontier molecular orbitals of the MSi15-BP compound (GMC-QDPT results)*

While the charge-transfer state is only slightly lower than the Si-chain absorption state for the ground-state structure of the MSi15-BP, the character of this state can be validated by other means. First, optimized structure of charge-transfer state shows fairly large gap between the two states. Second, the energy of the charge-transfer state is expected to be overestimated due to the environment interaction effects that are missing from the calculations of limited-length chain in vacuum. Lastly, the calculated lifetime of the S_1-S_0 transition (0.89 ns) is in good agreement with the PBMSi fluorescence lifetime (1.2 ns) which is itself unusual for this class of materials [44].

5.3. Excited-state relaxation of MSi15-BP

The relaxation scheme of MSi15-BP compound is presented in Fig. 5.3. It contains fast internal conversion between Si-chain absorption and charge-transfer states (corroborated by the located intersection point in the vicinity of the absorption structure), enhanced intersystem crossing between singlet and triplet CT states [45] and subsequent triplet conversion followed by emission from the lowest state of the biphenyl group.

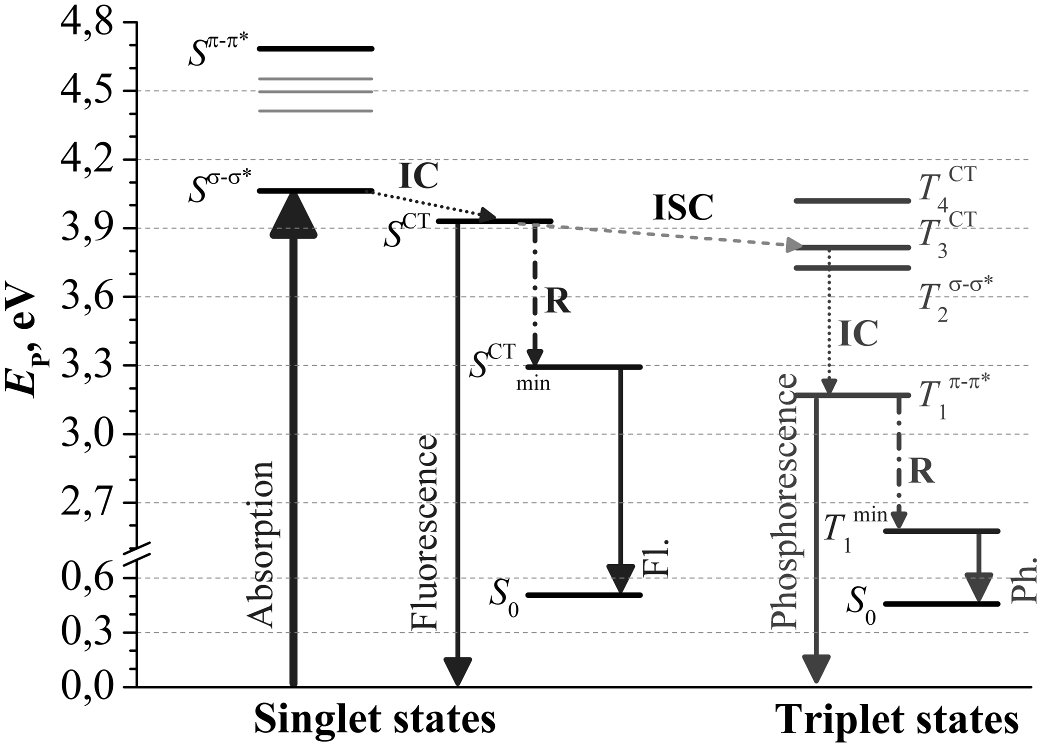

Figure 5.3. *Energy conversion scheme of MSi15-BP compound*

5.4. Energy conversion processes in PBMSi polymer

Calculated results of the electronic state structure of the MSi15-BP compound together with the performed experiments allow to explain most properties of the PBMSi polymer:

- The highest-wavelength absorption peak (340 nm) corresponds to the excitation of the Si chain.
- The initial fluorescence peak at 364 nm, which is characteristic for the silylene polymers [46], is replaced after a few ps by the red-shifted broader peak at 416 nm, which corresponds to the fluorescence from the charge-transfer state. The non-radiative conversion between two states is carried out through the intersection point of the two states.
- Phosphorescent emission at 460 nm (observed at low temperatures) is caused by the emission from the lowest triplet state of the biphenyl side-group. Other triplet states have higher energy and cannot quench this emission. However, it may still

be quenched by the external impurities and therefore might be not detectable at room temperature.

- The position of the charge-transfer state in the electronic spectrum, namely small positive singlet-triplet CT splitting, explains the striking efficiency of the phosphorescence [45]. The similar effect was recently observed for the intermolecular polaron pairs in CuPC:PCBM blends [47]. The internal conversion of triplet states takes place of the conventional polaron recombination in this case.

Therefore this study suggests a new molecular-level engineering approach for the enhancement of the ISC, enabling efficient conversion of primary excited singlets into triplets in conjugated polymers without involving heavy atom effect.

▼▼▼

6. Phosphorescence of the organometallic iridium complex

Even despite the drawback mentioned in the previous chapter, organometallic complexes are the most widely used triplet emitters for the organic semiconductor applications [48], because the triplet states can be efficiently populated by electric charge carriers and then emit photons with internal quantum efficiency close to 100 % [49]. However, despite the multitude of experimental and theoretical studies, technology of organic semiconductors is still young and has not reached its limiting potential [50].

Of the organometallic complexes used, the most popular are the iridium-based compounds because of the effective room-temperature emission [39] as well as long-lived excitations [51]. On the other hand, the excitation lifetime poses some difficulties as well, because in pure materials excitations might be quenched due to the annihilation processes [52]. To avoid this, the organometallic complexes are “diluted” by adding stable charge-carrier groups, for example, carbazoles [53]. The main task of the following study was to investigate the electronic spectrum of the organometallic iridium(III) complex, bis(phenylbenzothiazole)-Ir-acetylacetonate ($(pbt)_2Ir(acac)$), with and without the added carbazole groups.

6.1. Structural model and computational methods

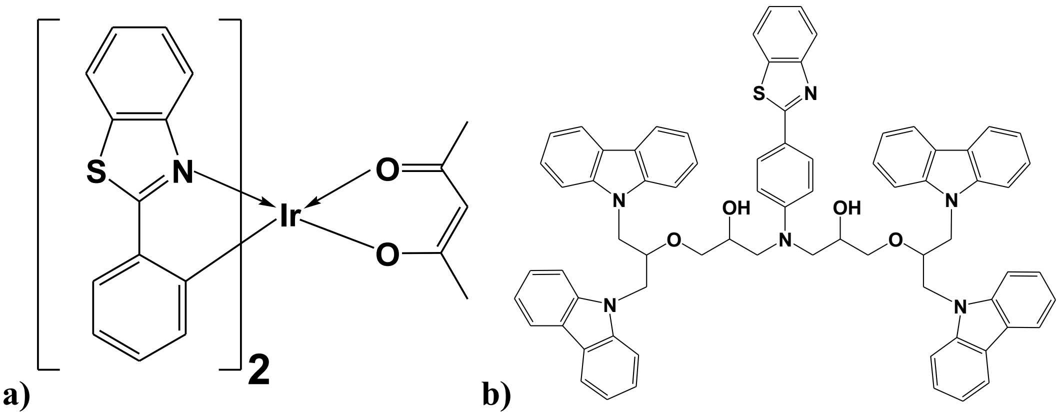

Figure 6.1. *Chemical structure of the investigated compounds: a) (pbt)$_2$Ir(acac) complex, b) pbt ligand with added carbazole groups*

Chemical structure of the (pbt)$_2$Ir(acac) compound and pbt ligand with added carbazole groups is shown in Fig. 6.1. The actual molecular structure of the compounds is more complicated (cf. sections 6.2, 6.3).

Time-dependent density-functional theory employing B3LYP functional and Lanl2DZ [54]/ 6-31G(d) basis sets was used for all calculations performed by *Gaussian03* package [6]. Continuum solvent model IEF-PCM [55] was used to include the effects of tetrahydrofuran solvent.

6.2. Properties of the absorption spectra

Theoretical absorption spectrum of the **pbt ligand** is presented in Fig. 6.2a, while the corresponding molecular orbitals are shown in Fig. 6.3. It is clear from the figures that the addition of the **carbazole groups** results in the red shift of the main absorption peak of the ligand because of the enlarged π system.

Addition of the charge-carrier groups to the entire photoactive complex changes only the position and height of the peak attributed to the separate ligand excitation (Fig. 6.2b), but not the lowest excitation of the complex, which includes the **iridium atom**. This indicates that the charge-carrier groups do not affect the optical properties of this compound.

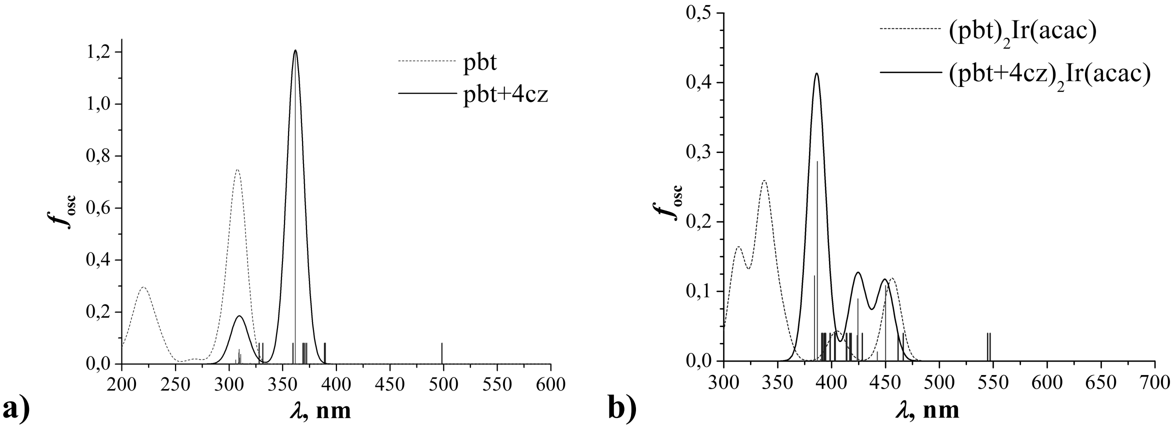

Figure 6.2. *The absorption spectrum of a) the 2-phenylbenzothiazole, b) the $(pbt)_2Ir(acac)$ complex, with and without the carbazole groups*

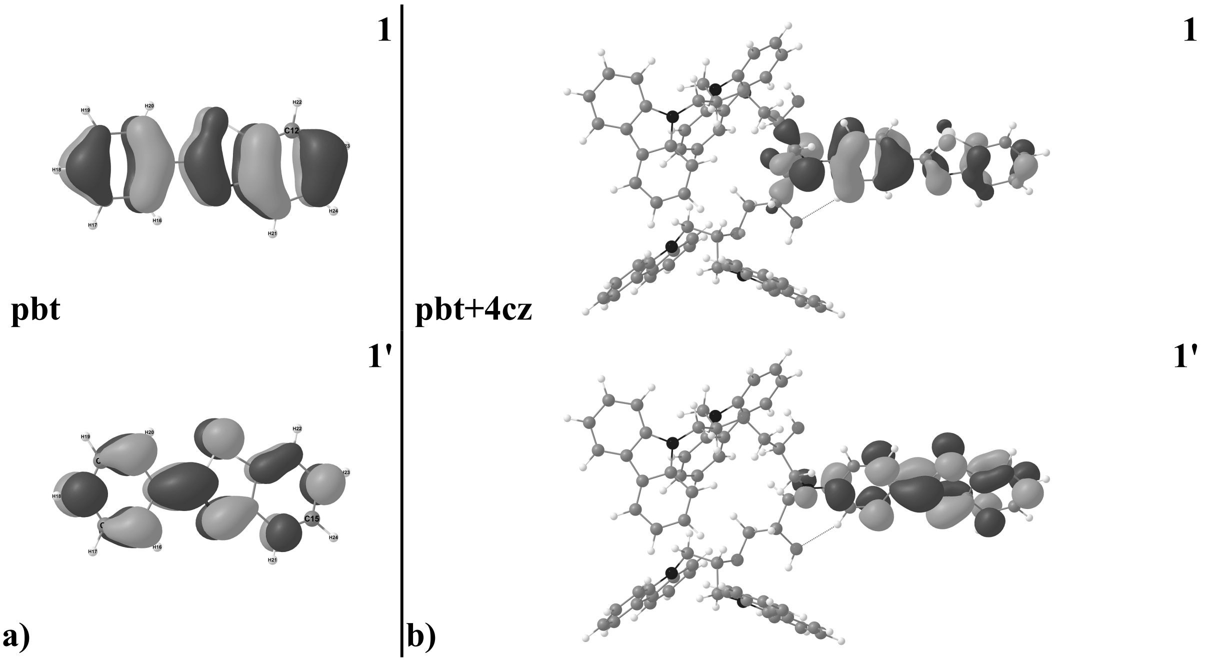

Figure 6.3. *Frontier molecular orbitals of the 2-phenylbenzothiazole (a) and with added carbazole groups (b)*

6.3. Structure and properties of the $(pbt)_2Ir(acac)$ complex

The geometric parameter optimization of the $(pbt)_2Ir(acac)$ compound results in the complicated structure shown in Fig. 6.4. The pbt ligands and acetylacetonate bridge surround the central iridium atom. Similar structures have been reported elsewhere [56]. This structure is very rigid; it does not change significantly between the optimized ground-state structure S_0 and the phosphorescent structure T_1. The main changes are observed in the parameters of one of the ligands. The changes break the symmetry of the complex, thereby inducing separation of the previously almost-degenerate energy levels (Fig. 6.5). As mentioned previously, addition of the carbazole groups does not have much influence on the properties of the lowest-lying excited states of the compound. On the other hand, the appearance of dark excited states corresponding to the carbazole-ligand electronic transitions indicates the possible mechanism of excitation transfer to the photoactive complex.

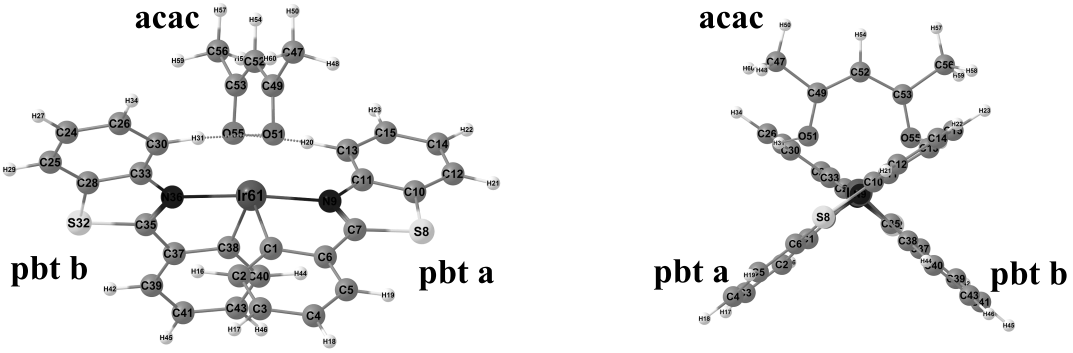

Figure 6.4. *Molecular structure of the (pbt)₂Ir(acac) complex*

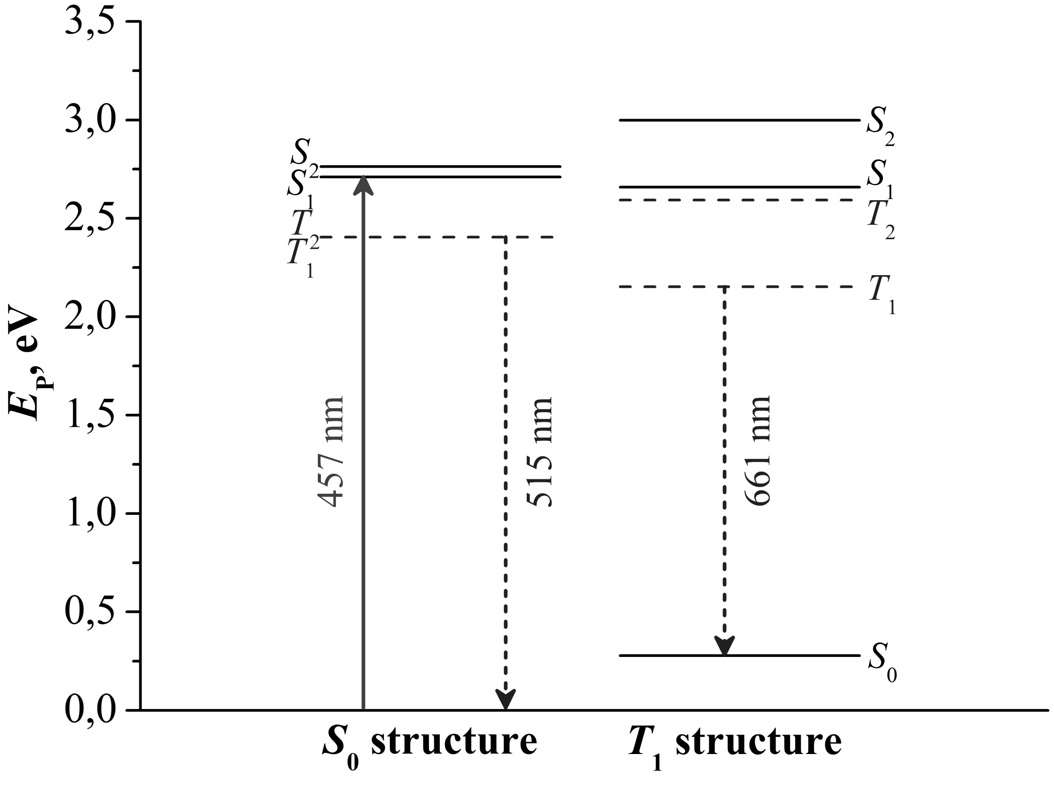

Figure 6.5. *Energy level diagram of the (pbt)₂Ir(acac) complex*

7. Conclusions

MIEP molecule

- MIEP molecule possesses two competing energy relaxation channels: excited-state emission and non-radiative relaxation through the intersection point on the potential energy surface.
- The polar solvent model predicts significant changes in the ground-state energy surface and is more favorable to the radiative conversion than the vacuum model.
- The main solvent effects are seen only when treating MIEP and adjacent solvent molecules as a supramolecular complex.

IB compound

- The chromophoric groups of the excited IB compound are formed in the different timescales due to the time needed for the conformational changes of the nitrophenol group.
- There exists an additional relaxation pathway without the significant structural changes that quenches the formation of the negatively-charged nitrophenolate.
- Shallow surface of the ground-state energy surface and low transition barriers are responsible for the thermal reversion of the IB compound to the initial state.

PBMSi polymer

- PBMSi polymer has low-lying singlet and triplet charge-transfer excited states that correspond to the electron density redistribution from the Si chain to the biphenyl group.
- The position of charge-transfer state is extremely favorable for the enhanced internal conversion and intersystem crossing in the material, leading to the efficient triplet population in the PBMSi polymer without heavy-metal effect.

$(pbt)_2Ir(acac)$ complex

- Differences between the absorption and phosphorescence states in $(pbt)_2Ir(acac)$ complex arise due to the symmetry-breaking structural changes in the ligands.
- The addition of the carbazole groups has no significant effect to the optical properties of the lowest-lying electronic states of the $(pbt)_2Ir(acac)$ complex.

8. The approbation of the conducted research

The results of the studies presented in the dissertation have been published in the following scientific papers:

1. S. Toliautas, J. Sulskus, L. Valkunas, M. Vengris, “Quantum chemical studies of photochromic properties of benzoxazine compound,” *Chemical Physics* **404**, 64–73, 2012.
2. S. Toliautas, M. Macernis, J. Sulskus, L. Valkunas, “Solvent effect on the photo-induced proton transfer in 2-(N-methyl-α-iminoethyl)-phenol,” *Chemical Physics Letters* **591**, 52–57, 2014.
3. A. Kadashchuk, Yu. Skryshevski, A. Vakhnin, S. Toliautas, J. Sulskus, R. Augulis, V. Gulbinas, S. Nespurek, J. Genoe, L. Valkunas, “Highly efficient intrinsic phosphorescence from a σ-conjugated poly(silylene) polymer,” *The Journal of Physical Chemistry C*, 2014 (under review).

The studies have been also announced in the following scientific conferences:

1. S. Toliautas, J. Šulskus, M. Mačernis, M. Vengris, L. Valkūnas, “Modelling of photochromic properties of benzoxazine compound by means of quantum chemical methods,” *ERPOS 12: Electronic and Related Properties of Organic Systems*, Vilnius, 2011 (poster).
2. S. Toliautas, J. Šulskus, K. Kazlauskas, S. Juršėnas, V. Getautis, L. Valkūnas, “Quantum-chemical calculations of novel phosphorescent iridium complexes,” *ERPOS 12: Electronic and Related Properties of Organic Systems*, Vilnius, 2011 (poster).
3. S. Toliautas, J. Šulskus, L. Valkūnas, „Benzoksazino junginio potencinės energijos paviršiai šviesa indukuoto sužadinimo metu“, *39th Lithuanian National Physics Conference*, Vilnius, 2011 (poster).
4. S. Toliautas, J. Šulskus, L. Valkūnas, “Modelling of structural and excitation properties of novel light-sensitive organic complexes,” *Vilnius Workshop on Nonlinear Spectroscopy and Open Quantum Systems*, Vilnius, 2011 (oral).

5. S. Toliautas, J. Šulskus, K. Kazlauskas, S. Juršėnas, V. Getautis, L. Valkūnas, "Modelling of excited-state properties of novel phosphorescent iridium complexes," *9th International Conference on Nanosciences & Nanotechnologies (NN12)*, Thessaloniki, 2012 (poster).
6. S. Toliautas, "Potential energy surface analysis of photochromic compound based on quantum-chemical computation," *Vilnius Workshop on Nonlinear Spectroscopy and Open Quantum Systems*, Vilnius, 2012 (oral).
7. S. Toliautas, M. Mačernis, J. Šulskus, L. Valkūnas, „Tirpiklio poveikis fotoindukuotai protono pernašai 2-(N-metil-α-iminoetil)-fenolio molekulėje", *40th Lithuanian National Physics Conference*, Vilnius, 2013 (poster).
8. S. Toliautas, J. Šulskus, A. Kadashchuk, Yu. Skryshevski, A. Vakhnin, R. Augulis, V. Gulbinas, S. Nespurek, J. Genoe, L. Valkūnas, "Highly efficient intrinsic phosphorescence from a σ-conjugated poly(silylene) polymer," *11th Nordic Femtochemistry Conference*, Vilnius, 2014 (poster).

Additional presentations by A. Kadashchuk:

9. A. Kadashchuk, Yu. Skryshevski, S. Toliautas, J. Sulskus, L. Valkunas, S. Nespurek, "Highly efficient intrinsic phosphorescence from a σ-conjugated polysilane polymer," *Baltic Polymer Symposium 2013*, Trakai, 2013 (poster).
10. A. Kadashchuk, S. Toliautas, J. Sulskus, R. Augulis, V. Gulbinas, S. Nespurek, L. Valkunas, "Highly efficient intrinsic phosphorescence from a sigma-conjugated poly(silylene) polymer," *ERPOS 13: Electrical and Related Properties of Organic Solids*, Swieradow Zdroj, 2014 (invited lecture).

About the author

Stepas Toliautas was born in 1985 in Vilnius. He attended S. Stanevičius secondary school. In 2003 he graduated the Vilnius Lyceum and entered the Faculty of Physics at the Vilnius University. There he obtained bachelor of physics and master of physics academic degrees (see below). In 2006, S. Toliautas studied for 5 months at the Linkoping University in Sweden through the Erasmus student exchange program.

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Education

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2003–2007	Bachelor studies, Faculty of Physics at the Vilnius University (study program “Computational Physics”)
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Stepas Toliautas

Elektroninio sužadinimo procesai fotoaktyviose organinėse molekulėse

Fotoaktyvios molekulės randamos beveik visose gyvosiose sistemose ir dalyvauja tokių reiškinių kaip fotosintezė bei rega metu. Be to, grįžtami fotoaktyvių molekulių struktūros pakitimai suteikia galimybę tokias molekules naudoti ypač mažo dydžio prietaisų konstravimui, o elektros ir šviesos energijos virsmai išnaudojami tobulinant organinės optoelektronikos elementus – organinius šviestukus bei saulės elementus. Minėti energijos virsmai teoriškai aprašomi kaip molekulės elektroninio sužadinimo dinamika, dėl kurios molekulė gali keisti struktūrą, spinduliuoti įvairaus bangos ilgio šviesą, sudaryti tarpinius tos pačios cheminės sudėties, tačiau skirtingų savybių fotoproduktus. Elektroninio sužadinimo dinamikos ypatybes įmanoma nustatyti tiesiogiai sprendžiant nenuostoviąją Šriodingerio lygtį elektroninei posistemei, tačiau toks metodas reikalauja ypač didelių skaičiavimo resursų ir šiandien tinka tik nedidelėms (kelių ar keliolikos atomų) molekulėms arba smarkiai apibendrintoms kvantinėms sistemoms. Kita vertus, sužadinimą bei tolesnius energijos virsmus įmanoma kokybiškai aprašyti sprendžiant nuostoviąją Šriodingerio lygtį skirtingoms molekulės branduolių padėtims ir nagrinėjant gautus pagrindinės bei sužadintų elektroninių būsenų potencinės energijos paviršius. Tokiu būdu galima tirti įvairaus dydžio ir struktūros molekulines sistemas bei gana skirtingos kilmės reiškinius. Tyrimų, pateikiamų daktaro disertacijoje, **tikslas** buvo elektroninės struktūros skaičiavimų metodais ištirti elektroninio sužadinimo sukeltus procesus keturiose fotoaktyviose organinėse molekulėse ir joms sudaryti sužadinimo relaksaciją apibūdinančius potencinės energijos paviršių modelius.

Pirmoji molekulė, MIEP, buvo tiriama siekiant modeliuoti bakteriorodopsino baltymo funkcinės grupės – Šifo bazės – optines savybes bei molekulei priklausančio protono pernašos eigą poliniame tirpiklyje. Tyrimo metu nustatyta, jog polinis tirpiklis pakeičia molekulės enol ir *cis*-keto atmainų (besiskiriančių protono padėtimi) stabilumą ir yra palankesnis *cis*-keto atmainai, kurios protonas prisijungęs prie Šifo bazės. Be to, po sužadinimo molekulės Šifo bazė deformuojasi ir sukelia tolesnę erdvinę protono pernašą. Nustatyta, jog tiesioginis tirpiklio molekulių įskaitymas deformacijos metu smarkiai pakeičia pagrindinės molekulės būsenos paviršių; tai nestebima naudojant elektrostatinį tirpiklio modelį. Gauti rezultatai kokybiškai atitinka panašaus junginio, MS1, etanolyje eksperimentais stebėtas savybes ir leidžia paaiškinti šios klasės molekulių ypatybes poliniuose tirpikliuose.

Antrasis tirtas junginys, indolo-benzoksazinas, pasižymi sudėtingomis fotochrominėmis savybėmis ir dėl atsparumo sužadinimo ciklų metu yra tinkamas molekulinių jungiklių kūrimui. Tyrimo metu buvo paaiškinti eksperimentiniai rezultatai ir nustatyta, jog junginio fotochromizmą lemia keli sužadinimo relaksacijos keliai, susiję su nitrofenolio grupės judėjimu indolo grupės atžvilgiu bei sąveika tarp grupių. Sukurtas modelis puikiai atitinka neseniai skelbtus kito išvestinio indolo-benzoksazino junginio eksperimentinių tyrimų rezultatus.

Trečiasis junginys yra silicio polimeras su prijungtomis organinėmis grupėmis. Šis junginys yra bene pirmas organinis konjuguotas polimeras, kuriame stebima naši žematemperatūrė fosforescencija nesant sunkiųjų metalų kompleksų ar kitų priemaišų. Bendradarbiaujant su keliomis eksperimentinėmis grupėmis nustatyta, kad už šią fosforescenciją yra atsakinga nedidelės energijos krūvio pernašos būsena tarp polimero silicio grandinėlės ir bifenilo šoninės grupės. Teorinis tyrimas pademonstravo, jog singuletinės ir tripletinės sužadintų krūvio pernašos būsenų padėtis energijos lygmenų spektre yra palanki ypač sparčiai interkombinacinei konversijai medžiagoje, dėl kurios efektyviai užpildomos tripletinės būsenos, iš kurių vyksta spinduliuotė.

Galiausiai buvo tirtas tradicinis metaloorganinis iridžio-ligandų kompleksas ir nagrinėta jo sąveika su funkcinėmis krūvininkų pernašos grupėmis. Nustatyta sudėtinga, nelanksti fotoaktyviojo komplekso struktūra, kuri sugerties metu yra beveik simetriška dviejų ligandų atžvilgiu, o fosforescencijos metu stebimi nedideli vieno iš ligandų struktūriniai pakitimai. Taip pat parodyta, jog prie ligando prijungtos karbazolių grupės šiek tiek sumažina ligando sugerties energiją, tačiau praktiškai nekeičia iridžio komplekso mažiausios energijos optiškai aktyvių elektroninių būsenų ypatybių.