Dr. Michał Filip Rode

Summary of Scientific Achievements

Theoretical optimization of properties of the molecular proton switch steered by optical or electrical field stimuli

Institute of Physics in Warsaw

Polish Academy of Sciences

Appendix 4

Summary of scientific achievements for the purpose of application for the degree „doktor habilitowany"

Warsaw, march 2019 Michał Rode

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1. PERSONAL DATA

Name and surname
Michał Filip Rode

Education and degrees

1998 – MSc in Chemistry, University of Warsaw, Faculty of Chemistry, Laboratory of Molecular Interactions, title of MSc theses: "Intermolecular Interactions in the Carbon Monoxide Dimer", Supervisor: Prof. Dr. hab. Joanna Sadlej.

2003 – PhD in Chemistry, University of Warsaw, Faculty of Chemistry, Laboratory of Molecular Interactions, Dissertation title: "The Structure and Infrared Spectra of weakly bound molecular clusters", Supervisor: Prof. Dr. hab. Joanna Sadlej.

Information on employment, scientific career

1998 – **2003** – PhD student, University of Warsaw, Faculty of Chemistry, Warsaw, Poland.
2001 – 3-month long pre-doc, *Jackson State University*, Jackson, Missisipi, USA.

2003 –**2004** – post-doc, Oakland University, Department of Chemistry, Rochester (Michigan), USA, Head of Laboratory: Prof. Małgorzata M. Szczęśniak.
2004 – **2005** – post-doc, *Faculty of Chemistry - Stuttgart University*, Stuttgart, Germany, Head of Laboratory: Prof. Hans-Joachim Werner.
2005 – **2013** – post-doc, Institute of Physics, Polish Academy of Sciences in Warsaw, Head of Laboratory: Prof. Dr. hab. Andrzej L. Sobolewski.
2013 – assistant, Institute of Physics, Polish Academy of Sciences in Warsaw.

2. SCIENTIFIC ACHIEVEMENTS BEING THE BASIS OF THE HABILTATION PROCEDURE

TITLE OF SCIENTIFIC ACHIEVMENT

Theoretical optimization of properties of the molecular proton photoswitch steered by optical or electrical field stimuli.

2.1. List of publications being the subject of habilitation, * - indicates corresponding author

H1. **M. F. Rode** and A. L. Sobolewski*, *Chem. Phys.*, 347 (**2008**) 413-421, "*Photophysics of inter- and intra- molecularly hydrogen bonded systems: Computational studies on the pyrrole-pyridine complex and 2(2'-pyridyl)pyrrole*". (IF2008 = 1.961, times cited: 25)

H2. **M. F. Rode***, A. L. Sobolewski, *J. Phys. Chem. A,* 114 (**2010**) 11879-11889, "*Effect of chemical substituents on energetical landscape of a molecular switch: an ab initio study*". (IF2010 = 2.732, times cited: 51)

H3. **M. F. Rode***, A. L. Sobolewski, *Chem. Phys.*, 409 (**2012**) 41-48, „*Ab initio study on the excited state proton transfer mediated photophysics of 3-hydroxy-picolinic acid*". (IF2012=1.957, times cited: 12)

H4. **M. F. Rode***, A. L. Sobolewski, *J. Chem. Phys.*,140 (**2014**) 084301-084314, „*Effect of chemical substitutions on photo-switching properties of 3-hydroxy-picolinic acid studied by ab initio methods*". (IF2014=2.952, times cited: 13)

H5. **M. F. Rode***, J. Jankowska, A. L. Sobolewski, *J. Chem. Phys.*, 144 (**2016**) 134303-134315, „*Ferroelectric molecular field-switch based on double proton transfer process: Static and dynamical simulations*". (IF2016=2.965, times cited: 2)

2.2. Introduction

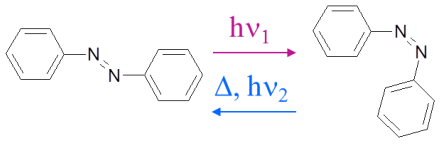
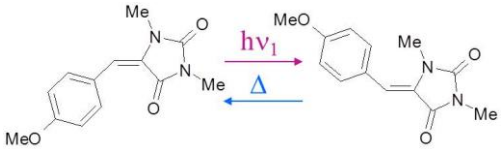
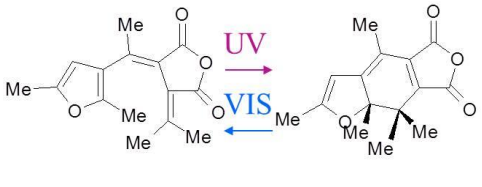
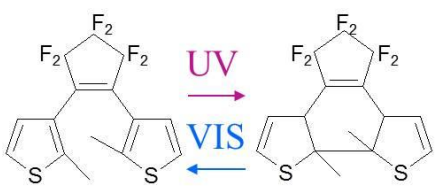
2.2.1. Search for functional molecules. From nano-cars to molecular photoswitches.

The Search for new functional materials, characterized with specific photophysical properties, is a hot research topic nowadays.[1-3] In 2016, Sauvage, Stoddart and Fering received the Nobel Prize in Chemistry for "the design and synthesis of molecular machines". As the Nobel Prize committee announced, the molecular machines, i.e. the nano-devices based on a single molecule, will be used in the near future in the development of modern materials, sensors and energy storage systems. Except for the nano-car driven and controlled by means of electrical pulses caused by the nano-needle of the scanning tunneling microscope, the molecular machines include also molecular elevators, rotors, photostabilizers or artificial muscles.

Search for functional materials is motivated by the need of designing and construction of modern devices, such as efficient light-emitting diodes (o-LED) or fast-excess memory chips

characterized by denser writing-capacity. The theoretical memory-writing capacity limits for silicon, as the material capable to store given memory size in the volume unit, will soon be reached out.[3] A new material, which could better serve as a memory cell than silicon, is then needed. The bottom-size-limit of the unit-memory-cell (1 bit) might be given by the size of the single photoswitchable molecule (the surface area of ~100 $Å^2$) which could replace the semiconducting silicon layer, in the future. The search for the molecular models characterized by nano-switchable properties can help in the implementation of these devices. Those switchable models are the bistable molecules having at least two (the best, if exactly two) stable forms[4]. The reversible switching of the two forms of the molecule may be triggered by any physical or chemical stimulus, such as applied external field (field switches),[5] electron transfer, chemical reaction, [6, 7] change of the reaction environment (e.g. pH),[8, 9] or optical excitation[10-12] (photoswitches). Such molecular photoswitches are present in the living organisms[13, 14] in which biological processes or reactions such as paralysis or vision process, may reversibly be induced when two different wavelengths of light: λ_1 and λ_2, are used to toggle the molecular switch between its two stable forms. Thus, a number of molecules – switches – is of importance to biochemistry[1] and medicine. [13, 15] It occurs that the ligands based on azobenzene – the photoswitchable molecule that change its shape upon UV light exposure (see Table 1) – were found to inhibit their adhesion to the surfaces when attached to

Table 1. Groups of compounds investigated in context of molecular photoswitches.

photoswitches based on rotation about the N=N or C=C double bond	
	
trans – cis Azobenzenes	*E – Z* Stilbenes (Hydantoin)[17]
photoswitches based on ring-opening or ring-formation processes	
	
Fulgide[18]	*Diarylethene*[19]

the bacterial organelles.[16] This photophysical property of the azobenzene molecule is brought into play e.g. in Alzheimer disease therapy when the photoswitchable molecule is

used as a transporter of the medicine toward the damaged amyloid peptide in the brain. [15]

2.2.2. Switches based on the proton transfer process.

Among the mechanisms of optical switching investigated so far dominated the ones which were based on the UV-light induced conformational changes and ring-closing/opening process in the molecules (Table 1). In the first group of mechanisms there is in particular a *cis-trans* isomerization in azobenzene and its derivatives that are called with generic name, *foldamers*.[20-22] In the second group we may mention the ring-opening processes observed in e.g. *fulgides*[18,23] and *diarylethenes*[19] in which the covalent bond was being broken (Table 1).

The switchable molecule, working as a memory cell, should be characterized by a relatively short time of the switching process between its two switching states which at the molecular level are denoted as the "stable forms". In this context, one of the drawbacks of the azobenzene- and stilbene-based[17] photoswitches is that the switching process, which involves rotation of the two moieties about the linking N=N or C=C double covalent bond in the excited state (S_1), is slow. Our attention was focused by the fact that there was limited number of studies devoted to switching mechanisms based on the process of transfer of proton – the least massive particle (except for an electron) – which process is one of the fastest in nature. An undesirable effect in azobenzenes is also the possibility of the thermal back-conversion of the *cis* form toward *trans* due to low-energy barrier between the forms in the ground electronic state (S_0).

It was shown lately that the proton transfer process may be induced by an electric field[24] in so-called field-switching systems [M13, see Appendix 5]. Those are the systems which are bistable when the field is not applied – the both forms of the system are separated with the low-energy barrier in the ground S_0 state. It occurred that in some molecules an electric field of large enough amplitude and applied in an appropriate direction may cause the barrierless proton transfer process along the intramolecular hydrogen bond and the population of one of the two forms of the system (while the second form of the system becomes completely depopulated). While applying the electric field in opposed direction causes the reverse process – the depopulation of the formerly populated form in favor of the population of the second one. In publication [H5], the ferroelectric field-switch molecule that could serve as an electric field sensor based on the phenomenon of the proton transfer in the S_0 state, was presented. In this case, the proton transfer process is induced by applying an electric field to the molecule in an appropriate direction.

The proton transfer process may also be triggered by light absorption, and take place in the excited electronic state, S_1, in the ESIPT process (Excited Intramolecular Proton Transfer) along the intramolecular hydrogen bond. This process is responsible for photostability of the system due to the fact that the proton transfer undergoing in the S_1 state in a barrierless manner leads toward the conical intersection region **CI(S_1/S_0)** between the excited S_1 and the ground S_0 electronic states. In the **CI(S_1/S_0)** geometry the nonadiabatic transfer process takes place between the two states thanks two which the excitation energy is dissipated into heat and the system returns to its nominal form in the ground state. This mechanism is responsible for photostability of the hydrogen-bonded molecules preventing them from photogeneration of undesired reaction photoproducts and thus it is widely used in commercial photostabilizers.[25]

Such features of the ESIPT process, ensuring photostability of the molecules and fast time of the process, were decisive to use by us in the modeling of the molecular photoswitches (the switching molecules for which the switching mechanism is based on the electron excitation). Those ideas were presented in publications [H2, H3, and H4, App. 5]. The molecular models of the photoswitches investigated by me for which the photoswitching mechanism is based on the ESIPT phenomenon are gathered in Table 5 in the summary section.

2.2.3. What is the optical molecular switch? The characteristic of the photoswitch at the molecular level.

The optical molecular switch is a molecule which when excited by light with the wavelength λ_1^{abs} (corresponding to the electronic excitation energy ΔE_1^{VE}) can permanently change its isomeric/tautomeric form. Further, this photogenerated form can also absorb the light quantum of different wavelength λ_2^{abs} (ΔE_2^{VE}) and drive the photophysical reverse process – recreating the nominal tautomeric form of the system. The process undergoes in the excited electronic state, S_1. Crucial for the process is here phenomenon of the light absorption that is manifested by an electron excitation of the molecule from its ground electronic S_0 state to one of the higher-energy electronic excited states, S_n. Such an electron transition, $S_0 \rightarrow S_n$, is characterized by a large absorption coefficient (oscillator strength *f*) that describes the probability of absorption of the light quanta. The electron excitation in the photoswitch molecule should be characterized by selectivity what requires the large enough difference between λ_1^{abs} and λ_2^{abs} (photochromism) to ensure the lack of overlapping of the respective electronic absorption bands of both the molecular forms. To characterize an ideal photoswitch

molecule one can impose additional conditions: (i) permanent switching demands that both forms of the molecule are separated by large energy-barrier in the ground S_0 state so that the only possible process leading to switching would undergo in the excited S_1 state. (ii) The S_1-state deactivation process should follow a barrierless pathway toward the conical intersection region **CI(S_1/S_0)** where the nonadiabatic transition, a radiationless excitation energy transfer should take place from the S_1 state to the nearby lying S_0 state. In this context, the ESIPT systems were very promising. (iii) The switching process should be reversible, i.e. the mechanism of the switching forth and back should be identical or be based on the same physical phenomenon. Additionally, it should be (iv) efficient and (v) fast. (vi) The photoswitching molecule should not undergo photodegradation processes so that it should be photostable. From the point of view of a potential application one form of the photoswitchable molecule should be characterized by kind of "action" and the other one by " the lack of action" – as in case of the memory cell – or by the presence or absence of a given property – e.g. possibility of the transport through membrane, or ability to surface adhesion, as in case of bacterial organelles.

2.2.4. Description of the scientific achievement.

In this report, I present the history of my scientific inquiries regarding the molecular modeling of various devices based on a single molecule. Among them, the most important position is occupied by the molecular optical switch, the mechanism of which is based on the proton (hydrogen atom) transfer in the excited state. The scientific achievement described in the series of publications [H1 – H5] is related to innovative use of theoretical quantum-chemical calculations in the search for molecules with the specific photophysical properties. Nowadays, quantum-mechanical calculations are a relatively cheap tool for pre-selection of molecules with specific properties in comparison to the cost of chemical synthesis and purification of these molecules. Such a methodology of research work can significantly accelerate the synthesis of the proper molecule.

Quantum-chemical calculations allow us today not only to calculate the potential energy surface (PES) in the electronic ground state, S_0, but also in the excited state, S_1, as well as to estimate the energetic barriers in both states. And this allows one to predict whether a given modification of the pattern molecule has a chance to speed up the process – when in a result of its application the energy barrier disappears – or even to slow it down – when the barrier grows. The series of publications is opened by publication [H1] in which, by means of the quantum-mechanical calculations, the phenomenon of double emission experimentally

observed for the 2 (2'-pyridyl) pyrrole (**PlPy**) molecule has been explained. The study of the photophysics of this molecule and the mechanism of the excited-state deactivation, which resembles the features of known molecular photostabilizers, resulted in the idea of such structure modification of the **PlPy** molecule so that the photophysical properties of the newly formed molecule would allow for its use as an optical molecular switch.

Motivation to carry out this type of research was from the very beginning the conviction that testing various types of chemical modification of a given molecule of potential properties – e.g. photoswitching – may be important in an optimization of its functionality. Innovation is based on a consequent modification of the structure of a given molecule aimed at obtaining the desired landscape of the potential energy surface (PES) of the electronic singlet states: S_0 and S_1, to improve the photophysical mechanism of switching. In this search, I proposed a number of molecular systems as well as various modifications in their structure [H2, H3, and H4]. For the first time in the literature the effect of substitutions[26, 27] was studied on the electronic excited states. Then, I used the results of these explorations and gained experience to modify the structure, which resulted in the improvement of the photophysical photoswitching mechanism based on the reaction energetics.

I will present here the basic assumptions of the operation of the optical molecular switch based in particular on the ESIPT process and describe the possible molecular mechanisms of optical switching that I have studied in a series of my publications: [H2], [H3] and [H4], as well as in several publications that I co-authored ([P1]… [P8], see Appendix 5). Next, I will present my own ideas and achievements in the use of the substituent effect to improve the functionality of some molecules in order to obtain optimal switching properties. Other methods of modification of the molecular structure that could generally be called molecular modeling directed to the functionality of the molecule or molecular system will also be discussed. One of such functionalities, studied in the past by prof. Andrzej Sobolewski, is photostability of molecules. This feature is fundamental for the optical molecular switching systems studied by me.

In the last publication [H5] from the series, a model of a molecular electric field sensor sensitive to the change of the field's magnitude and direction was presented. In this publication, the mechanism of the double proton transfer process steered by applied an electric field is described. Examining this issue, I used both the stationary *ab initio* calculations and the "on the fly" molecular dynamics simulations. What publications [H3] and [H5] have in common is the discussion of changes in the mechanism of double transfer of

the proton caused be the electronic excitation or the magnitude and direction of the applied electric field in the molecule.

2.2.5. Theoretical methods used in the calculations.

In the performed quantum-chemical calculations we tried to reproduce or predict the photophysical properties of the multi-atom and multi-electron molecules, which are the subject of our research, as best as possible. For this reason in quantum-chemical calculations, we could not use the most sophisticated methods that are usually used for small systems in their electronic ground state. The methods that were used first of all, ensure good agreement with experiment and allowed to get results in a reasonable time and. In addition, it should be said that calculations for the excited state are definitely more demanding in terms of the computing time and the memory used compared to the calculations for the ground state. Therefore in my research, I had to accept a compromise between the use of a sophisticated calculation method and the time devoted to calculations in both electronic states of the investigated molecule.

***Ab initio* methods used in the calculations.** In the case of the calculations for the ground state (S_0) the Møller–Plesset perturbation theory of the second order (MP2[28]) was used. In the MP method, the solution of the Schrödinger equation in the approximation of the Hartree-Fock method (HF) is used as a reference single-determinant wave-function. The same wave-function obtained in the HF method is used in the coupled cluster method (CC). Its limited version for single and double excitations (CCSD,[29] S-singles, D-doubles) was used in publication [H5] as a kind of pattern to justify the correctness of choosing the electron density functional method (DFT, [30] Density Functional Theory) for the studied system. The CCSD method is very demanding and time-consuming (is scaling like N^6 with the number of the basis functions, N). Therefore, in the calculation of the excited states (S_n) of multi-electron and multi-atom systems its simplified version, the second order approximate coupled cluster model with simplified amplitudes for single and double excitations (CC2)[31, 32] is commonly used. The CC2 method, like CCSD, limits the energy calculations to the double excitations from the HF references, but it is much faster and scales like N^5.[31]

The weakness of the CC2 method (as well as of any single-reference method) is the problem in a description of the geometry of the systems with the near-lying energy levels, such as the geometry of conical intersection **CI(S_1/S_0)** for which the wave function, by definition, becomes multi-reference. In order to more accurately describe such intersections of the two

states, we need to go beyond the single-electron approximation and use the multi-configurational method of the self-consistent field for complete active space (CASSCF,[33] Complete Active Space Self-Consistent Field). While both the post-HF methods: MP2 and CC2, take into account the dynamic correlation of electrons in the description of the considered electronic state of the system, the CASSCF method does not include it. However, it better describes the biradical geometries. The dynamic correlation, however, is important in the description of electronic excitations, when the proper description of the absorption or emission spectra of molecules is needed. Therefore, the CC2 method was used in an optimization of the geometry of the systems in the excited states.

Recently another method, ADC(2)[34, 35] (algebraic diagrammatic construction method of the second order) was implemented that enables calculations for the electronic excited states. It gives better convergence near the conical intersection regions **CI(S_1/S_0)**. This method was used in the last few publications of my co-authorship.

An alternative method for multi-atom systems is the Time-Dependent DFT method (TD-DFT). This method in combination with standard electron density functionals fails, however, in the case of the excited states with a strong CT (charge-transfer) character, especially when correlation-exchange functionals (xc) are used.[36] The energies of excitations are significantly underestimated, over 1 eV, and the energy profiles of the CT states are defective,[36] as a result of improper 1/R dependence along the coordinate describing the separation of charge R.

In the last publication [H5] from the series, we wanted to compare the results of static calculations with the results of molecular dynamics simulations. We also wanted to get information about the time of the double proton transfer process as a function of the applied electric field. The adiabatic "*on-the-fly*" molecular dynamics was used either for the molecule placed in the electric field or for the molecule in the absence of electric field. In this dynamic calculations, the wave function calculated at the DFT level was used with the B3LYP[37] correlation-exchange potential because calculations at this level of theory allowed for the influence of the electric field to be taken into account.

atomic basis sets used in the *ab initio* calculations. The predicted energy of the electron excitations in the CC2 method is usually overestimated by approx. 0.3-0.5 eV.[38] This estimation error can be reduced when using a larger atomic basis set, also one that contains diffuse functions. For example, the use of the aug-cc-pVDZ basis set is important in the correct description of the Rydberg excited states. In practice, to keep a reasonable calculation time, I often used a smaller atomic basis set, e.g. Dunning's cc-pVDZ[39] basis set (a

correlation consistent basis set with a double-split valence shell containing polarization functions), to optimize the geometry of the ground state, and then a larger basis set, aug-cc-pVDZ,[39] containing also diffuse functions, for calculating the absorption spectrum for these geometries. The same procedure is used to calculate the emission spectrum when we use the geometry of the molecule optimized in the excited electronic state.

Program packages used in calculations. To perform calculations for the purpose of publications described here, various packages of calculation programs were used. Most calculations were done using the TURBOMOL program package,[40] which offers an implemented CC2 method used by me to calculate properties of the excited states, such as absorption and emission spectra as well as the excited-state energy profiles in [H1 – H5] and the ADC(2) method, which was also used by me for this purpose in many other publications. In order to determine the correct geometry of conical intersections **CI(S_1/S_0)**, the CASSCF method implemented in the Gaussian 03 and 09 package[41] was used. On the other hand, in publication [H5] the molecular dynamics simulations for the description of the double proton transfer process in a molecule placed in an electric field was carried out using the Newton-X program.[42, 43] The program was compatible with the TURBOMOL program package.

2.3. Photoswitches based on a single molecule controlled by optical excitation.

2.3.1. Comparison of photophysics of the photostable systems with inter- and intra-molecular hydrogen bond on the example of pyrrole - pyridine complex and the 2 (2'-pyridyl)pyrrole molecule (publication H1).

Research motivation: The motivation to undertake research in publication [H1] was the willingness to compare the two mechanisms of the excited-state proton transfer: in the van der Waals complex – EDPT (Electron-Driven Proton Transfer) – and in the molecule – ESIPT (Excited-State Intramolecular Proton Transfer). This was done for the two systems composed of the same subunits: pyrrole (**Pl**), as the proton donor, and pyridine (**Py**), as the proton acceptor. One system, the complex (**Pl**–**Py**), was connected with the intermolecular hydrogen bond, and the second one, the 2(2'-pyridyl)pyrrole molecule (**PlPy**), with the intramolecular hydrogen bond. Both the proton transfer mechanisms in the S_1 state are responsible for the photostability of commercially available molecular photostabilizers, such as TINUVIN[25] and nucleobases in DNA.

The proton transfer mechanisms: ESIPT (in the molecule) and EDPT (in the complex).

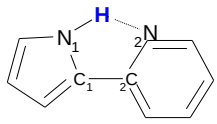
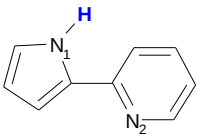
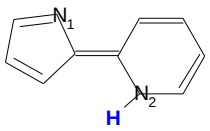
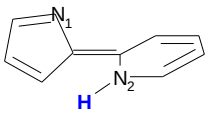
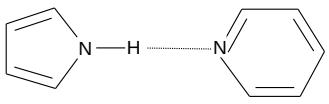
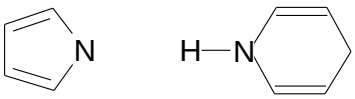
Absorption of light by the system results in an electron excitation from the electronic ground S_0 state to one of the higher excited states, S_n (where the transition $S_0 \rightarrow S_n$ is characterized by high oscillator strength, *f*). This process causes a change in the electron density distribution in the absorbing system. In terms of description of the electronic structure methods, the electron excitation is the transfer of an electron from the orbital occupied in the ground state (e.g. HOMO, Highest-Occupied Molecular Orbital) to the virtual, unoccupied higher-in-energy orbital (e.g. LUMO, Lowest-Unoccupied Molecular Orbital). Those two orbitals, however, look a bit different in the molecule and in the molecular complex. In the **PlPy** molecule, the π(HOMO) and π∗(LUMO) orbitals are delocalized on the whole molecule. In the **Pl-Py** complex, however, in which the subsystems are separated, both the π(HOMO) and π∗(LUMO) molecular orbitals are localized on one of the two molecules: pyrrole or pyridine that are separated. Thus, the valence electrons in the **Pl-Py** complex are localized on the pyrrole or pyridine molecules. In the **Pl-Py** complex, the absorption can induce an electron locally – within one molecule unit, e.g. pyrrole (**Pl**). Then we talk about the locally excited state, S_1^{LE}(**Pl,Pl**). In case of the electron excitation from pyrrole (**Pl**) to pyridine (**Py**), we talk about the excited state with the charge transfer character, S_1^{CT}(**Pl,Py**). In this S_1^{CT} state, the π(HOMO) orbital is localized on the pyrrole and the π∗ orbital (LUMO) on the pyridine molecule. The S_1^{LE} state (**Pl, Pl**) is an associative state – it pulls the proton back to the pyrrole nitrogen atom. While the S_1^{CT} state is a dissociative state – it allows the proton to move in a barrierless manner toward the pyridine nitrogen atom following the electron that already is occupying the LUMO π∗ orbital on pyridine. The EDPT process occurs when the non-adiabatic transition from S_1^{LE}(**Pl,Pl**) to S_1^{CT} (**Pl,Py**) takes place. This demands overpassing the excited-state energy barrier for the proton transfer reaction.

In order to better understand the ESIPT mechanism in the **PlPy** molecule, the analysis of the electronic configuration of the S_1-state tautomeric forms of the molecules involved in the PT process was performed. This analysis shows that during the evolution of the PT process, the electron is transferred from the π (HOMO) orbital, being delocalized on the whole **PlPy** molecule, toward the π∗ (LUMO) orbital, which is only initially delocalized on the entire molecule, and as the PT reaction progresses, it becomes more and more localized on the pyridine moiety. The ESIPT process has, therefore, a diabatic character – the transfer of a proton along the hydrogen bond is coupled with the flow of electron density along the

molecule from the side of pyrrole (acting as a photoacid) toward the pyridine side (acting as a photobase).

Barrierless access to the conical intersection geometry CI(S_1/S_0) from the Franck-Condon region as a guarantee of the photostability of the system. Both mechanisms, EDPT and ESIPT, may be the reason for the photostability of the complex and molecule. A common feature of both photostability mechanisms is that the system in the S_1 state along the coordinate describing the transfer of the proton follows toward the area of the conical intersection **CI(S_1/S_0)**. In the **CI** geometry, the non-adiabatic transfer of the excitation energy from the S_1 state toward the S_0 state takes place that is followed by the return to the original form of the system. What differentiates the two mechanisms are the geometrical parameters that define the reaction coordinate. In the case of the **PlPy** molecule, the ESIPT reaction coordinate involves first, the stretching of the N_1H bond (dissociation of the proton from the pyrrole nitrogen atom and associating it by the pyridine nitrogen atom) and next, the rotation of the protonated pyridine with respect to the pyrrole moiety around the main axis of the molecule given by the C_1-C_2 bond (see Table 2).

Table 2. Tautomeric forms of the PlPy molecule and the forms of the van der Waals Pl-Py complex that are built from the pyrrole and pyridine molecules.

PlPy molecule			
			
a) syn(ea)	***b) anti***(ea-r)	**c) tautomer *anti***(kb)	**d) *min*^{S1} ~ CI (S_1/S_0)**
Pl-Py compleks			
			
pyrrole **pyridine**		**pyrrole** **pyridine**	
global minimum		**CI(S_1/S_0)**	

In order for the **Pl-Py** complex to reach the **CI(S_1/S_0)** geometry, except for the elongation of the N_1-H bond distance that approaches the proton toward the pyridine nitrogen atom, the pyrrole and pyridine molecules must additionally elongate for a considerable distance R_{N1-N2} ~4 Å. Separation of the pyrrole and pyridine molecules allows for the occupation of the strongly polar S_1^{CT} state which in a barrierless manner brings the system closer to the **CI** region. Both in the case of the **PlPy** molecule and **Pl-Py** complex, the **CI(S_1/S_0)** geometry is

the global minimum of the S_1 open-shell singlet state, as both unpaired electrons occupy two orbitals that are orthogonal (are not overlapping) – the HOMO orbital is localized on the pyrrole, while the LUMO orbital on the pyridine molecule indicating biradical structure of **CI**. Instead, the **CI** geometry is extremely unstable in the S_0 state, because both electrons in this state are trying to occupy the lower-energy HOMO orbital which is located on the pyrrole molecule and therefore when the system is in the S_0 state the proton is pulled back by the pyrrole N_1 nitrogen atom.

Scientific achievements of publication H1:

a) Double fluorescence as a consequence of the presence of the S_1-state energy barrier for the proton transfer in the PlPy molecule.

In a typical ESIPT system, the proton transfer process is exoenergetic and barrierless in the S_1 state. However, in the **PlPy** molecule, we have identified the presence of a low-energy barrier (~ +0.2 eV) for the transfer of the proton in the S_1 state from the ***syn***^{S1}(ea) form toward **s*yn***^{S1}(eb). From the point of view of the shape of the potential energy landscape of the S_1 state, it is an important observation that in the **PIPy** molecule the intramolecular hydrogen bond closes the 5-membered pseudo-ring. Today's knowledge, gained also from the subsequent publications: [H2], [H3], [H4], indicates that similar systems – the ones that have the imidazole moiety instead of pyrrole in their structure – also have a barrier to the transfer of a proton, and it is associated with a fairly long hydrogen bond (H◦◦◦Y) in the systems with a 5-membered ring. This binding is longer than in case of the systems with a 6-membered ring in which the ESIPT process occurs most often in a barrierless manner from the proton donor – a photoacid (e.g. the –OH group in 7-hydroxyquinoline [H2], 3-hydroxypyridine [H3], [H4], or 2-phenol [P3, P7, App. 5]) toward the photobase, i.e. the part accepting the proton in the S_1 state. The atoms which most often attract the proton in the S_1 state are nitrogen atoms – present in the 6-membered heterocyclic rings, such as pyridine, oxazine and similar [H3],[44] – or oxygen atoms – present in the aldehyde group [H3], [P2], [P5], [P6] and its derivatives,[45, 46] or the carboxylic group [H3, H4]. This information was crucial for me in modeling the compounds with the properties of the ESIPT photoswitches mentioned above and tested in the publications: [H2], [H3], [H4], [P1-P3, P5-P7]. The systems with the 5-membered ring, therefore, have an energy barrier to transfer the proton in the S_1 state due to the occurrence of higher steric strain compared to systems with the 6-membered ring in which the process is usually barrierless. The question about the existence of a barrier is of great importance when

interpreting fluorescence spectra. Thanks to the estimation of the energy-barrier in the S_1 state we were able to assign experimentally measured dual emission values for the **PlPy** molecule: the blue: Fl_1 – from the ***syn***^{S1}(ea) form and the red: Fl_2 – from the ***syn***^{S1}(eb) tautomer.[47, 48] Both the emitting forms and emission transitions: Fl_1 and Fl_2, observed from these forms are marked with colored vertical arrows in Fig. 1.

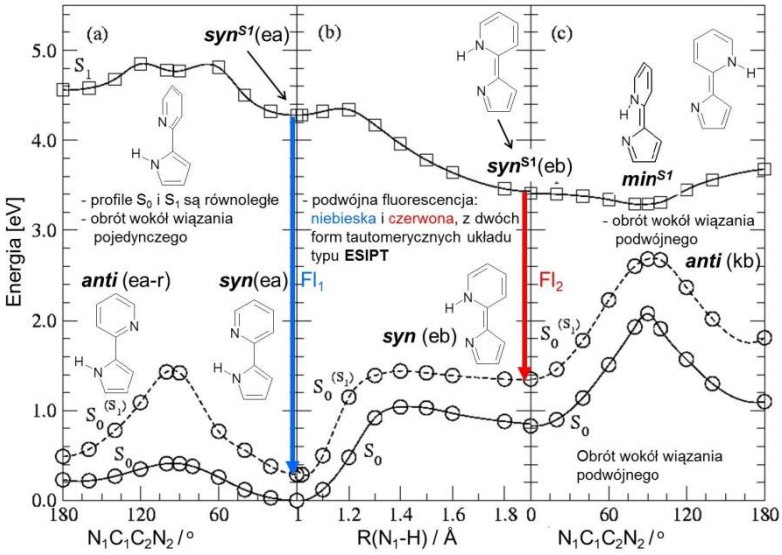


Fig. 1. Photophysics of the **PlPy** molecule and the landscape of the potential energy surface of the S_0 and S_1 states. The low-energy barrier (estimated with the CC2/cc-pVDZ method), separating the two energetic minima in the excited S_1 state explains experimentally measured double emission: the blue Fl_1 and red Fl_2.

b) Prediction of the shape of the energetic profiles in the excited S_1 state depending on the number of covalent bonds around which the molecule is rotated.

From the point of view of scientific achievement, the most important conclusion from publication [H1] is knowledge about the variation of the energy profiles of the excited S_1 state as a function of the corresponding coordinate describing the reaction. In particular, it is a coordinate describing the rotation of subsystems (or a functional group) in a molecule around a bond of a given bond-order. The conclusions of this analysis are as follows: (i) When two rotamers are connected with the rotation around a single bond (rotamers: ***syn***(ea) and ***anti***(ea-r) of the **PlPy** molecule, Fig. 1.a – left panel), one can expect a certain energy barrier in the S_1 state for the geometry twisted by ~ 90^o around the C_1-C_2 bond. Similarly, one can expect a low barrier in the ground S_0 state (~ 0.2 eV) for rotation around this bond. As a consequence, the photogeneration of the ***anti***(ea-r) form by excitation of the ***syn***(ea) form in the S_1 state is rather difficult (Fig 1a). (ii) When two stereoisomers are connected with the rotation around a double bond (isomers ***syn***(eb) and ***anti***(kb) of the **PlPy** molecule, Fig. 1.c – right panel), one can expect a high energy barrier in the S_0 state for the geometry twisted at ~ 90^o (~ 1 eV), thanks to which the anti (kb) form is stable. In the S_1 state, however, both the ***syn***(eb) and ***anti***(kb) stereoisomers are unstable because the optimization of their geometry relaxes toward

the S_1-state minimum with the twisted geometry around the C_1=C_2 double bond at an angle of ~ 90^o. This effect is called ethylenic behavior because in the ethylene molecule rotation around the double bond is possible only after electron excitation. It turns out, that as a result of light absorption the C_1=C_2 bond is getting longer in the S_1 state, i.e. it becomes *de facto* single and the rotation around it becomes also easier, which we have examined in the publication on photoswitches based on the 7-hydroxyquinoline molecule (**7HQ)** [H2], [P5]. Let us finally note that the double bond between the C_1 and C_2 atoms in the **PlPy** molecule is formed not sooner the transfer of the proton occurs from the pyrrole N_1 to the pyridine N_2 atom to form the tautomeric ***syn***(eb) form (Fig. 1. b). That's why the carried out observations could have been made for this molecule.

Conclusions from publication [H1]. The most important conclusion from publication [H1] is that we can predict the shape of the excited state potential energy profile with the order of the bond around which the rotation takes place. In the case of a double bond in the S_0 state, one can expect a shallow profile of the potential energy in the S_1 state or even an appearance of a minimum in this state. However, in the case of the rotation about a single bond, the appearance of the energy-barrier can be expected in both states.

This observation was used in many subsequent publications for modeling the photo-switches based on the ESIPT process [H2, H3, H4, P7], gathered in Table 5 [P1-P3, P5-P7, App. 5]. Knowledge about the rotation around single or double bonds in the S_1 state was used to study the mechanism of the process of nonradiative deactivation of the excited state in natural dyes, betaxanthins [M14, App. 5], what is also the subject of my current scientific investigations, as well as in the study on extremely interesting photophysics of the 3*H*-naphthopyran molecule (publication in preparation).

The mechanism of nonradiative deactivation of the excited state in the **PlPy** molecule and in the **Pl-Py** complex differs in two main aspects. The most important difference is the character of the PT process. In the case of a molecule, the proton transfer process in the S_1 state is adiabatic; The proton follows the electron along the intramolecular hydrogen bond, while the electron, in turn, moves along the valence bonds within the molecule. However, in the **Pl-Py** van der Waals complex, this process is nonadiabatic because it requires a nonadiabatic transition between the S_1^{LE} and S_1^{CT} states which means a sudden change in the electron density or sudden jump of an electron between the molecules. In the case of the **PlPy** molecule, it was possible to attribute experimentally observed double fluorescence to the two emitting excited-state forms of the molecule and explain this phenomenon by the energy-

barrier separating these forms in the excited state. The proficiency in predicting the shape of the energy profiles of the ground and excited states based on the order of bonds around which the rotation of the molecule takes place is very important. The shape of the potential-energy profiles and the height of the energy barriers have a tremendous impact on the competition of light-induced processes.

Finally, it should be added that the **PlPy** molecule, as having a deeper S_0-state minimum in the ***anti***(kb) form in comparison to previously tested systems like TINUVIN, has become a prototype of an optical molecular switch based on the systems with a single hydrogen bond – in the salicylidenemethylamine (**SMA**) molecule [P3] and its derivatives [P7, App. 5]. Those molecular photoswitches were developed by a PhD student of Prof. Andrzej Sobolewski, MSc Joanna Jankowska, for whom I also provided scientific guidance from 2011 to 2014. Those studies resulted in several publications.

2.3.2. Photoswitching mechanism based on the ESIPT process assisted by the twist of the proton crane (publication H2).

The shape of the energy profile of the **PlPy** molecule suggested that after applying some modifications to its structure there is a chance to obtain a new molecule with the photoswitching functionality (as defined in Section 2.2.3). In this context, the ***anti***(kb) form of the **PlPy** molecule (Fig. 1.c) has too high relative energy which does not allow this form to be permanently kept in thermodynamic equilibrium with the nominal form, ***syn***(ea). This high relative energy, ~ 1 eV, results from the lack of an atom or functional group in the pyrrole ring capable to attract the proton by forming a hydrogen bond with it on the opposite side of the **PlPy** molecule. In addition, the results of publication [H1] indicated that one should strive for modeling a molecule in which the hydrogen bond would be engaged in the 6-membered ring, which would provide barrierless access to the **CI(S_1/S_0)** area in the S_1 state. Based on this knowledge, the theoretical model of the 7-hydroxy-8-oxazine-quinoline[44] molecule (**7HQ_ox**), proposed by Prof. Andrzej Sobolewski, became the prototype of a new class of photoswitches, **TPT** (TWIST-assisted ESIPT), which I managed to design. The general model of the molecule acting as the molecular photoswitch belonging to the **TPT** class is shown in Fig. 2. The molecule of the **TPT**-class photoswitch, as in the case of the photostabilizer,[25] consists of the two subunits: a molecular frame (**F**), acting as a proton donor, and the proton crane[49] (**C**). The frame **F** and the crane **C** are connected by a single covalent bond. Let us note, that in comparison with the photostabilizer molecule, such as **PlPy**, an additional **Z** atom is built in the frame **F** which together with the **X** atom are the two proton donor-acceptor

centers located on the two opposite sides of the photoswitch in order to ensure the stability of its two tautomeric forms, so-called "states of the switch": $\mathbf{S_0^a}$ and $\mathbf{S_0^d}$ (Fig. 2). The **TPT**-type photoswitching mechanism between the two tautomeric forms of the molecule is based on the

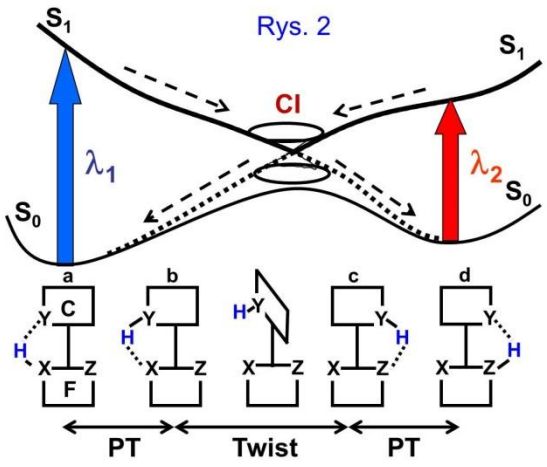


Fig. 2. The **TPT**-class photoswitching mechanism based on the ESIPT proces assisted by the twist of the proton crane leading toward the geometry of the conical intersection **CI(S_1/S_0)**.

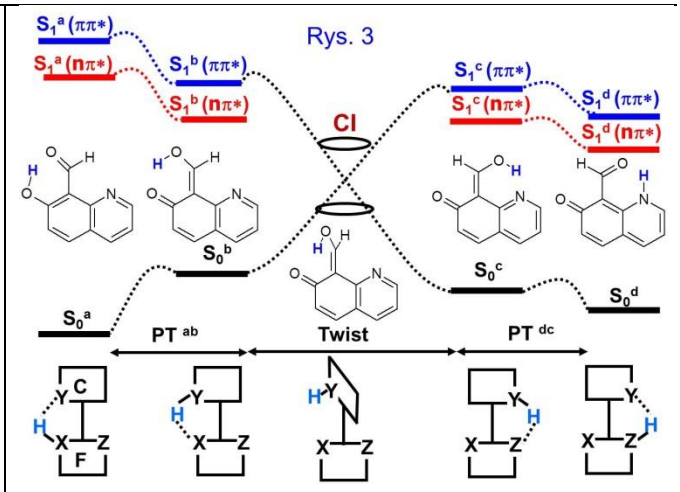
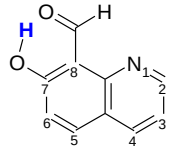
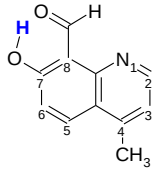
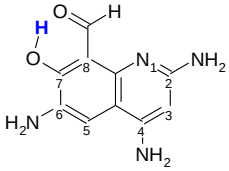
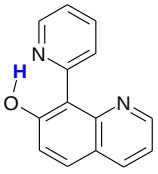
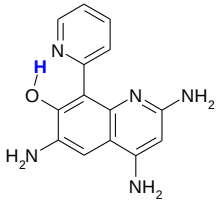


Fig. 3. The 7-hydroksy-8-aldehydo-chinoliny molecule (**7HQ-CHO**) as an example of realziation of the **TPT**-class photoswitch. Tautomeric forms of the molecule in different electronic states: S_0, $S_1(n\pi^*)$ and $S_1(\pi\pi^*)$.

long-range transfer of the proton H between the two distant atoms, **X** and **Z** (where **X**, **Z** = O or N). The photoswitching is carried out via a twist motion of the proton crane **C**, acting as a proton transmitter between the two "states" of the photoswitch: $\mathbf{S_0^a}$ and $\mathbf{S_0^d}$. For this purpose, the proton crane **C** has only one proton acceptor-donor center, the **Y** atom, which after the photoexcitation is able to attract the proton associated with one of the two tautomeric forms. Next, the crane is able to rotate with this proton (TWIST motion) and return it to the **X** or **Z** atom of the molecular frame **F** by switching to the second state of the system. The photoswitching process is initiated by light absorption which induces the transfer of the proton in the S_1 state, ESIPT, from the molecular frame **F** to the proton crane **C**. Because the photoswitching of one form to another takes place with the assistance of the rotation of the two parts of the system (TWIST) – the crane **C** *vs*. the frame **F** – we classify this mechanism as **TPT**. Twisting of the molecule is necessary to reach the geometry of the conical intersection **CI(S_1/S_0)** (Figs 2 and 3). In this way, we create a class of the **TPT** proton photoswitches, shown in Fig. 2. The main example of this photoswitch type is the 7-hydroxy-8-carbaldehyde-quinoline molecule (**7HQ-CHO**) proposed by me (Fig. 3). In this molecule, the 7-hydroxyquinoline molecule (**7HQ**) acts as the molecular frame, while the aldehyde group, –CHO, acts as the proton crane. The **7HQ** frame has the two spots able to accept the proton: the 7-OH group (the enol switch form) and the quinoline nitrogen atom, N (the keto

form). As a result of light absorption, the proton H is transferred from the oxygen atom of the 7-OH hydroxyl group or from the quinoline nitrogen to the oxygen atom of the aldehyde group, –CHO, of the crane to create the $\mathbf{S_1}^{\mathbf{b}}$ excited-state form in the $\mathbf{PT}^{\mathbf{ab}}$ process (left panel Fig. 3) or the $\mathbf{S_1}^{\mathbf{c}}$ form in the $\mathbf{PT}^{\mathbf{dc}}$ process, respectively (right panel, Fig. 3). As a result of this process, a significant rearrangement of the single and double valence bonds occurs in the structure of the **7HQ-CHO** molecule; The single bond connecting the –CHO crane with the **7HQ** frame becomes the double bond in the S_0 state. As a result of this rearrangement high S_0-state energy barrier occurs that separates both "states" of the photoswitch. In the S_1 state, however, the connecting bond is elongated resembling a single bond. Thus, the rotation about this bond becomes easier, enabling barrierless access to the $\mathbf{CI(S_1/S_0)}$ region in the S_1 state (center Fig. 3). In this geometry a nonadiabatic transition to the S_0 state takes place. As soon as the system is in the S_0 state, the crane dissociates the proton H which can next be attracted back by the C=O group, recreating the initial $\mathbf{S_0}^{\mathbf{a}}$ form, or by the nitrogen atom photogenerating the tautomeric $\mathbf{S_0}^{\mathbf{d}}$ form. The reaction coordinates that can describe the $\mathbf{PT}^{\mathbf{ab}}$ and $\mathbf{PT}^{\mathbf{dc}}$ processes are therefore the respective O-H and N-H distances. The $\mathbf{PT}^{\mathbf{ab}}$ reaction connects two tautomeric forms: "**a**" with "**b**"; similarly, $\mathbf{PT}^{\mathbf{dc}}$ connects the tautomeric forms: "**d**" with "**c**". The rotameric forms "**b**" and "**c**" are related to each other by the rotation of the protonated crane **C** with respect to the molecular frame **F** (central panel). In order to measure and compare the energetic effect for the given **PT** process, we defined the enthalpy of the respective reaction, ΔH_r^{ab} and ΔH_r^{dc}, as the energy difference in the excited state between the respective forms $\mathbf{S_1}^{\mathbf{a}}$ and $\mathbf{S_1}^{\mathbf{b}}$ (for ΔH_r^{ab}), $\mathbf{S_1}^{\mathbf{d}}$ and $\mathbf{S_1}^{\mathbf{c}}$ (for ΔH_r^{dc}). The exemplary ΔH_r values for the chosen investigated **TPT**-class photoswitches are given in Table 3. It is worth paying

Table 3. Molecular models of the TPT-class photoswitches discussed in this work.

7HQ-CHO [H2]	**4M-7HQ-CHO** [P2, H2]	**2,4,6-tri-NH_2** [H2]	**pyridine** [H2]	2,4,6-tri-NH_2 **+ pyridine** [H2]
				
ΔH_r^{ab} = -0.38 ΔH_r^{dc} > +0.4	ΔH_r^{ab} = -0.37 ΔH_r^{dc} > +0.4	ΔH_r^{ab} = -0.66 ΔH_r^{dc} = -0.74	ΔH_r^{ab} = -0.75 ΔH_r^{dc} = -0.08	ΔH_r^{ab} = -0.93 ΔH_r^{dc} = -0.96

attention particularly to the change in the sign of the ΔH_r^{dc} enthalpy for the series of compounds presented. The ΔH_r^{dc} enthalpy is positive, signaling the endoenergetic reaction,

for the unsubstituted compound, **7HQ-CHO**, and negative, indicating exoenergetic reaction, for the 2,4,6-triamino-substituted compound as well as with the pyridine in function of the crane.

Requirements for the molecular structure for an effective TPT photoswitching mechanism. The switch molecule, schematically shown in Fig. 3, can generally have four stable tautomeric forms in the S_0 state and four stable forms in the S_1 state. In addition, the characteristic feature of typical hetero-aromatic systems is the presence of low-lying excited states: $S_1(n\pi^*)$ and $S_1(\pi\pi^*)$. These states can be easily distinguished by symmetry when the system is planar. Such an assumption is justified when we consider the process of transferring a small particle – a proton whose motion is very fast compared to the other vibrational movements of the system. Therefore, to study and describe the photophysics of the **TPT**-type molecular optical switch, 12 photophysically relevant forms of such molecule should be examined; four in each state: S_0, $S_1(n\pi^*)$ and $S_1(\pi\pi^*)$, see Fig. 3.

The transfer of the proton from the molecular frame toward the crane should cause a corresponding rearrangement of valence bonds in the molecule so that the protonated crane can rotate along the barrierless S_1-state energy profile. In addition, the experience gained from [H1] showed that the system in which the intramolecular hydrogen bond forms a five-membered ring with the heterocyclic system indicates a certain barrier to the transfer of the proton in the excited state. To make the lack of such a barrier more probable, it is necessary to model the molecule that forms an intramolecular hydrogen bond within a 6-membered ring. These considerations led to the conclusion that the 7-hydroxyquinoline molecule, **7HQ**, having two donor centers - oxygen (**X**) and quinoline nitrogen (**Z**), would be an ideal candidate for the molecular frame **F** of the switch (Fig. 3). On the other hand, the proton crane **C** should also form the 6-membered ring together with the frame **F**. Therefore, in the prototype switch, **7HQ_ox**,[44] the oxazine molecule was used as the proton crane. Unfortunately, the synthesis of the **7HQ_ox** molecule has not been successful so far, despite the attempts of synthesis of this molecule by the chemist from our research group. It is a great pity because the **7HQ_ox** molecule is characterized by an ideal landscape of the excited-state potential energy surface, S_1-PES, mainly due to the barrierless path leading toward the **CI(S_1/S_0)** area along the S_1-state profile from both the excited-state forms of the **7HQ_ox** photoswitch molecule.

Argon-matrix isolation Experiment [**P2**]. What is my own idea in modeling the **TPT**-photoswitch, is the use of the carbaldehyde group, –CHO, as the proton crane [H2] in the **7HQ-CHO** molecule. The **7HQ-CHO** molecule is presented in Fig. 3. The idea was based on

the fact that the –CHO group, being lighter than oxazine, should result in a shorter time of twisting with respect to the molecular frame. The idea occurred to be good also due to that the derivatives of the **7HQ-CHO** molecules occurred to be relatively easy to be synthesized. The synthesis was done by the chemist from our scientific group, Dr. Jacek Nowacki. Thanks to his success in synthesis of the methyl derivative of **7HQ**, the 7-hydroxy-4-methyl-8-carbaldehyde-quinoline molecule (**4M-7HQ-CHO**) [P2, App. 5] (see Table 3) was the first photoswitching molecule studied experimentally. This molecule was used in the low-temperature argon-matrix isolation experiment in which the sample was irradiated with UV light. Exposure products were identified using infrared spectroscopy (IR). The system, being in its nominal form, $\mathbf{S_0^a}$, was irradiated with light with a wavelength corresponding to the maximum of its absorption. As a result of this process, the photoproduct $\mathbf{S_0^d}$ was created which has been identified. Then, the photoproduct $\mathbf{S_0^d}$ was irradiated with its characteristic wavelength corresponding to its absorption maximum. As a result of the second UV-light exposure, part of the nominal $\mathbf{S_0^a}$ form population was repopulated. An important result of this study [P2] was that for the first time the reversibility of the photo-switching process based on the **TPT** mechanism, i.e. the long-range proton transfer within a single molecule, was confirmed experimentally.

This experiment was inspired by my theoretical studies on the **7HQ** derivatives as potential molecular photoswitches [H2]. My contribution to the publication [P2] was to perform *ab initio* calculations and determination of the energy profiles for the **4M-7HQ-CHO** molecule (see Fig. 5 in publication [P2]). It was the shape of these energy profiles that explained why full reversibility of the photoswitching process was not possible in the matrix isolation experiment. Especially important occurred to be the presence of the substantial energy-barrier in the $S_1(\pi\pi^*)$ state for the $\mathbf{PT^{dc}}$ process of the transfer of the proton from the quinoline nitrogen to the oxygen atom in the –CHO crane that was found to be the reason for incomplete reproduction of the $\mathbf{S_0^a}$ form during the back-photoswitching process. It was due to the fact that there was found the large energy-barrier in the $\mathbf{PT^{dc}}$ process separating the S_1^d form from the $\mathbf{CI(S_1/S_0)}$ region (Fig. 3). It should be noted, that there is no such barrier for the analogous $\mathbf{PT^{ab}}$ process – the transfer of the proton from the oxygen atom of the 7-OH group (at the position C_7) toward the oxygen atom of the –CHO group. This reaction turned out to be exoenergetic for the vast majority of the **7HQ-CHO** derivatives in later studies [H2]. Some of those were also experimental studies [P5 and P6] which were inspired by the suggestions contained in theoretical publication [H2]. The analysis of the shape of the potential energy profiles of the **H4-7MQ-CHO** molecule determined by me allowed to identify two main

drawbacks related to the landscape of the PES surface of the **PT^{dc}** reaction for this molecule of the potential photoswitch nature:

1) The main drawback that turned out in the study was that the **PT^{dc}** reaction in the $S_1(\pi\pi^*)$ state is endoenergetic ($\Delta H_r^{dc} > 0$) towards the "**c**" form, and has an energy barrier toward the **CI(S_1/S_0)** geometry (see right side Fig. 3).

2) The second disadvantage was that the $S_1(n\pi^*)$ state was lying below the $S_1(\pi\pi^*)$ state along the entire potential energy profile as a function of the N_1H coordinate describing the PT^{dc} reaction. The $S_1(n\pi^*)$ state was lying below the $S_1(\pi\pi^*)$ state also for both forms: **S_1^a** and **S_1^d**.

Modeling of the TPT-class photoswitch molecule based on the 7HQ molecular frame. What is needed to be improved in the mechanism of the H4-7MQ-CHO molecule? (publication H2).

The main goal of publication [H2] was to find such modifications of the chemical structure of the **7HQ-CHO** molecule (Fig. 3, Table 3) that could induce the desired changes in the potential-energy profiles of the **7HQ-CHO** derivatives; (i) They would increase the exoenergeticity of both the **PT^{ab}** and **PT^{dc}** proton transfer processes in the S_1 state in the direction of the **CI(S_1/S_0)** geometry, and (ii) they would reduce or get rid of the S_1-state energy barrier in the **PT^{dc}** process, if possible. I would like to point out, that while I expected that by means of appropriate structure modifications it would be possible to change the potential energy profile of the ESIPT processes, I did not know whether it would be possible to cause that the process would take place in a barrierless fashion in the S_1 state. Especially, that the energy-barrier for the **PT^{dc}** reaction in the **7HQ-CHO** molecule was high, $\Delta H^{dc} > 0.4$ eV (Table 3). I decided to choose the already known **7HQ** molecule as the molecular frame of the photoswitch. The **7HQ** molecule was very convenient due to many possible substitution positions: C_2, C_3, C_4, C_5, and C_6. These positions could be used for substitutions with chemical groups of various electron-donating/accepting character. The position 1 was occupied by the quinoline nitrogen atom, N_1, which could attract the proton; the C_7 position was substituted with the proton donating hydroxyl group; while the C_8 position was used to substitute the proton crane **C** that was the –CHO group, at the first stage of the study. To analyze the results, I used the pEDA scale (π-electron donor-acceptor parameter) for different substitutions presented by Ozimiński and Dobrowolski.[26] The scale allows distinguishing the π– and σ–electron-donor (EDG) or acceptor (EWG) character of the substituent. This gave me an additional information about

the substituent effect depending on the nature of the excited state I have studied: $S_1(\pi\pi^*)$ or $S_1(n\pi^*)$. An additional motivation was the fact that this scale was created for the ground state, while my original idea was to check, firstly, whether the scale allows predicting the properties of the excited state and how it affects the stabilization of the appropriate minima. Secondly, whether the effect exerted by a substituent with certain π– or σ– EWG / EDG properties is different for the $S_1(\pi\pi^*)$ and $S_1(n\pi^*)$ states. It seems to me that no one so far has put the issue of the ordering of the $S_1(\pi\pi^*)$ *vs*. $S_1(n\pi^*)$ states as the result of the substituents used. It is important in such a context, that in addition to the orbital nature the $S_0 \rightarrow S_1(\pi\pi^*)$ electron transitions are usually strongly allowed, while the $S_0 \rightarrow S_1(n\pi^*)$ transitions are forbidden or poorly allowed (they have a low *f* value). Therefore, the molecules being in the $S_1(n\pi^*)$ state usually do not emit radiation and thus are spectroscopically invisible. However, in studying the photophysics of aromatic molecules it is important whether the $S_1(n\pi^*)$ state is lower or higher than the respective $S_1(\pi\pi^*)$ state. For example, the $S_1(n\pi^*)$ state can quench the emission[50] (as it was demonstrated in [M14]) as well as inhibit the process, e.g. ESIPT, which could occur in the reactive $S_1(\pi\pi^*)$ state, but it does not, because of the energy-barrier existing in the lowest $S_1(n\pi^*)$ excited state in the system. [51]

Conclusions from publication [H2]. I have shown that by using the substituent effect one can modulate the PES surface of the excited S_1 state for the optical **TPT** molecular switch. This finding can be successfully extended to other functionalities of the molecules. I have shown that the excited state is susceptible to the substitution of the π–/σ–electron-donating/accepting groups and that this effect is analogous to the effect known and studied so far for the ground electronic state. In particular, it was shown that a methyl group has only a negligible effect on the energetics of the excited state (the methyl group, $–CH_3$, is a very weak electron donor in the S_0 state). On the other hand, an amino group with a strong π-electron-donating and a strong σ-electron-accepting character is able to stabilize the $S_1(\pi\pi^*)$ excited states with respect to the $S_1(n\pi^*)$ excited states when this group is substituted to the **7HQ** frame in the so-called "hot positions": C_2, C_4 or C_6. In addition, it was stated the qualitatively additive character of multiple substitutions to the **7HQ** frame in relation to the enthalpy of both the ESIPT processes. When all three amino groups were substituted at the C_2, C_4, and C_6 positions, thus obtained the 2,4,6-triamine-7-hydroxy-8-carbaldehydequinoline molecule occurred to be the first derivative to show a barrierless ESIPT process aimed at the conical intersection **CI(S_1/S_0)** area from the region of Franck-Condon simultaneously for both forms:

enol "**a**" and keto "**d**" (Table 3). Either this system or the 2,6-diamino-substituted derivative are recommended for synthesis as molecules with potential photoswitching properties due to the exoenergetic ESIPT processes and with an additional feature of destabilization of the $S_1(n\pi^*)$ state with respect to $S_1(\pi\pi^*)$. A similar effect can be reached by systems substituted by other groups with a strong π-electron-donating character: e.g. dimethylamine (–DMA) or hydroxyl (–OH).

In order to obtain the correct landscape of the PES surface of the S_1 state and therefore the correct functioning of the photoswitch, it is also important to choose an appropriate proton crane unit. The 6-membered heterocyclic rings should work better as the proton crane than the aldehyde group, –CHO. This conclusion can be drawn from the analysis of the shape of the excited-state potential energy profile. The reason for this is that such rings are better electron acceptors. Therefore, the perfect photoswitch should be made of the **7HQ** molecular frame to which one substitutes the π-electron-donating groups in the "hot positions" and use the proton crane unit that is able to withdraw electrons from the molecular frame.

Quantum-mechanical calculations of the reaction profiles along the relevant internal coordinates of the **TPT** type switches suggest that the photoswitching process should be reversible for a series of molecules containing 7-hydroxyquinoline (**7HQ**), as the frame of the switch, and oxazine[44] [H2], pyridine [P1], [H2] or other 6-membered heterocyclic rings [H2] (Y = nitrogen), as well as an aldehyde group, –CHO [H2], [P2], [P5], [P6] or the aldehyde group substituted with a dihydroborane, $–CO\text{-}BH_2$[46] (Y = oxygen), as the proton craning functional group.

The studied substituent effect on the shape of the potential-energy profiles of the $n\pi^*$ and $\pi\pi^*$ excited states and elaborated methodology of the structure modification developed in publication [H2] were both used in the dissertation of MSc Joanna Jankowska investigating an analogous group of photoswitches based on the **SMA** molecule and its derivatives and the **TPT** mechanism by means of theoretical methods. In this research area, except for the doctoral dissertation, two publications were published which I co-authored [P3, P7]. I have also used this methodology in publication [H4] devoted to the new photoswitching mechanism. MSc Jankowska continued research on the **SMA** molecule for which she performed molecular dynamics simulations. The results of her work allowed her to estimate the time-scale of the total photoswitching process from the substrate to the product at ~ 145 fs. Time of ~ 30 fs was devoted for the ESIPT process and ~ 115 fs for the twist around the C=C double bond (TWIST).[52]

The results of publication [H2] found a considerable response in the publications citing it in various contexts, first of all, (i) the optical switch[45, 46, 53, 54] and second,(ii) the substituent effect.[27, 55, 56] The work was a motivation for attempts to synthesize new compounds – derivatives of 7-hydroxy-8-carbaldehydequinoline (with the –CHO group as the crane). The derivatives of the **7HQ-CHO** molecule substituted at the 2-methyl, 2,4-dimethyl, 2-phenyl, and 2-methoxy positions were synthesized and their photoswitching properties described in publications [P5] and [P6]. While the 4-methyl derivative was studied in publication [P2].

In publication [P5], the differences in photophysics of the derivatives of the **7HQ-CHO** molecule substituted at the C_2 position by the neutral (methyl) and the strong π-electron-donating (methoxy) group were confirmed using the spectroscopic methods in the context of the height of the S_1-state energy barrier on the transfer of the proton from the form $\mathbf{S_1^d}$ to $\mathbf{S_1^c}$. The results of the substituent effect could have been correlated with the scale of electron-donating/accepting, pEDA parameter. The pEDA scale was predicted also by means of the quantum chemistry methods just before publishing [H2].[26]

2.3.3. Photoswitching mechanism based on the double proton transfer in the excited state mediated by the proton transmitter unit (publications H3, H4).

Genesis of the idea of the photoswitch based on the double proton transfer in the excited state (DPT). In the **TPT** type photoswitching mechanism discussed above, the single proton was transported within the molecule using the twisting movement of the proton crane. Rotation of the two heavier subunits with respect to each other usually takes more time than the movement of the proton particle itself. The time-scale of the entire photoswitching process for the 7-Hydroxy-8-morpholinomethyl-quinoline **TPT**-type switch molecule, was estimated experimentally for hundreds ps (using the transient absorption spectroscopy with subpicosecond resolution time (300 fs) using UV pulses (340 nm)[53]. For this molecule, the dynamics of the proton transfer from the enol to the keto form was studied. However, one should remember that morpholinomethyl unit, used here as the proton crane, is a cyclic saturated hydrocarbon, i.e. it is unconjugated with the **7HQ** frame. Even if the time-scale of the photoswitching process in the system with the conjugated crane would be below 1 ps, it is quite long compared to the anticipated time for the ESIPT process (<50 fs).[52] That is why a new photoswitching mechanism was proposed by me in which the twisting motion of the crane was replaced by the process of the double proton transfer (DPT) in the S_1 state (Fig. 4). The mechanism based on the transfer of the two protons toward the two different sites along the two hydrogen bridges was denoted here as **DPT**. In the **DPT** photoswitch, the proton

crane moiety was replaced with the chemical group acting as a proton transmitter unit. The proton transmitter moiety, like the proton crane, is connected with the molecular frame of the

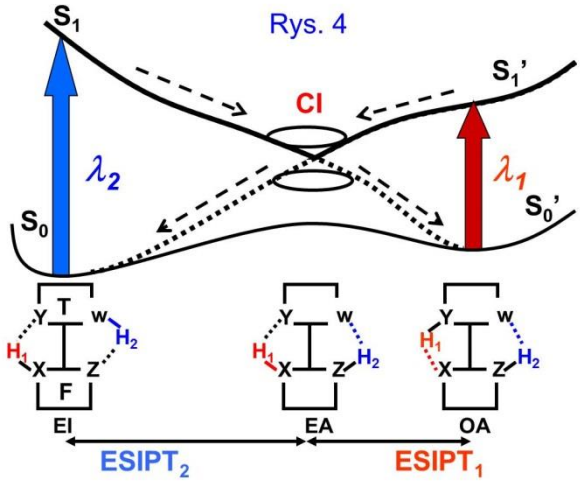
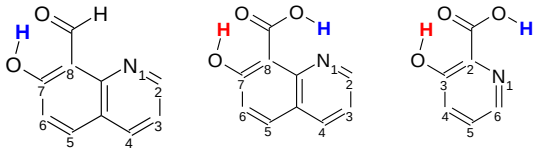


Fig. 4. **DPT-class** Photoswitching Mechanism based on the double proton transfer process in the excited state mediated by the proton transmitter unit (T). The photoswitching process follows the path leading toward the conical intersection area **CI(S_1/S_0)**.

photoswitch with a single covalent bond. The proton transmitter has two additional atoms: **Y** and **W** (and not one - as in the twisting proton crane), that both can accept or give away the proton. These atoms form two hydrogen bridges in the molecule: **X**H_1⋯**Y** and **W**H_2⋯**Z**, with the **X** and **Z** atoms built in the molecular frame of the photoswitch. Such a model allows direct double ESIPT process in the S_1 state along these two hydrogen bridges by sequential transfer of the two protons. My attention was focused to the 7-hydroxyquinol-8-carboxylic acid molecule (**7HQ-CA**) for which the **DPT** process was confirmed experimentally to take place in the S_1 state.[57] The **7HQ-CA** molecular structure (Table 4) differs from **7HQ-CHO** (Table 3) only by the presence of the carboxyl group, –COOH, substituted at the C_8 position of the **7HQ** frame.



7HQ-CHO **7HQ-CA** **3HPA**

Table 4. The molecules discussed in publication [H3]. Enumeration of atoms in a given molecular model. The protons invoked in the hydrogen bonds are indicated with color.

The –COOH group is able both to accept the proton (present in the 7-OH group) by the oxygen atom of the carbonyl group and to dissociate the proton present in the COOH group to give it away to the quinoline N_1 nitrogen atom. Therefore, this molecule seemed to fit perfectly into our model of the **DPT**-class photoswitch, because the carboxyl group is well suited as the proton transmitter unit. Unfortunately, the analysis of the potential energy surface of the ground state of the **7HQ-CA** molecule (as well as its excited state – data not yet published) showed that the double-proton-transferred minimum, **OA**, (Fig. 4) is highly

energetic and shallow in the S_0 state and is separated by a very low energy-barrier from the most stable **EI** form. Therefore, I decided that the **7HQ-CA** molecule is not promising as an optical switch in which we should have two stable forms separated by a relatively high energy barrier in the ground state. Therefore, we decided to reduce the aromatic system from the two rings to one and examine the photophysics of the 3-hydroxy-picolinic acid molecule (**3HPA**) (Table 4). The advantage of the **3HPA** molecule over **7HQ-CA** is based on the longer lengths of hydrogen bonds spanned between the proton-donating/accepting atoms: **X**◦◦◦**Y** and **W**◦◦◦**Z**, thanks to which the two stable forms of the potential switch were more likely to be separated by a higher energy-barrier in the S_0 state.

Photophysics of the 3HPA molecule (publication H3).

The landscape of the potential energy surface of the ground state of the 3HPA molecule.

Therefore, the **3HPA** molecule occurred to be a good model to start a detailed study on its photophysics in terms of potential photoswitching properties of the **DPT** class. The results are discussed in [H3]. The **3HPA** molecule (Fig. 5) possesses two stable tautomeric forms: **EI**(S_0)

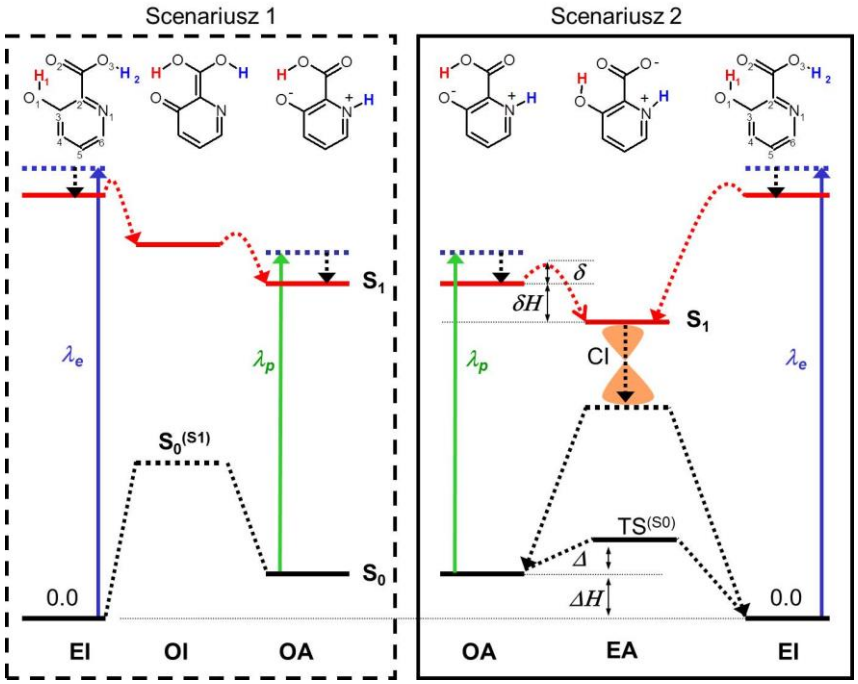


Fig. 5. Tautomeric forms of the **3HPA** molecule. The two scenarios of the double proton transfer process. Illustration of the photophysical parameters of the **DPT**-class photoswitch. The nπ* state forms (red), the ππ* state forms (blue).

and **OA**(S_0), stabilized by two intramolecular hydrogen bonds: O_1-H_1◦◦◦O_2 and O_3-H_2◦◦◦N_1, which enforce the planar geometry of the system. Both tautomers differ in their position of the two protons distinguished by color: H_1 and H_2. The **EI**(S_0) tautomer is the most stable form of the **3HPA** molecule. The less stable form, **OA** (S_0), with the two transferred protons lies +0.44 eV above the global **EI**(S_0) minimum (MP2/cc-pVDZ) and is separated from it by a relatively high energy-barrier, +0.34 eV. The double proton transfer reaction path is separated

by the transition-state geometry, **TS**(S_0), corresponding to the **EA**(S_0) saddle point (see Fig. 5 and Fig. 1 in [H1]) in which the carboxylic group is deprotonated and both the H_1 and H_2 protons are attached to the pyridine molecular frame of the switch. This means that the process of double transfer of the protons in the S_0 state between the two forms of the **3HPA** molecule does not occur synchronously (then the transfer of both protons would be simultaneous) but can be classified as an asynchronous 1-step process (with one energy-barrier in the **TS**(S_0) geometry) – corresponding to the reaction in which one proton is transferred at a time and then it is followed by the transfer of the second proton.[58] The UV-absorption spectrum is different for both forms of the molecule; It indicates on photochromism of both the stable forms. The difference in the lowest vertical excitation energies, ΔE^{VE}, is of ~ 1eV. In the context of photoswitching, this gives a very good excitation selectivity for both forms of a potential photoswitch. Another desirable parameter was high energy-barrier separating both forms in the S_0 state. What was an undesired parameter was the value of the relative energy of the less stable **OA**(S_0) form. I focused my attention on improving this parameter in publication [H4] in which I proposed a modification of the system aimed at stabilizing the **OA** form in relation to the **EI** form in the S_0 state. The desired effect of improving this parameter was reached by the substitution of the **3HPA** molecule by the amino group, $–NH_2$, at the C_4 position as well as the insertion of the additional nitrogen atom into the pyridine ring at the C_6 position.

The landscape of the potential energy surface of the ππ* and nπ* excited states for different forms of the 3HPA molecule. The landscape of the S_1-state PES of the **3HPA** molecule is much more diverse than that of the S_0 state. There are two tautomeric forms in play: **OI**(S_1) and **EA**(S_1) (Fig. 5), which both mediate the process of the double proton transfer according to two different scenarios caused by the excitation of one of the photoswitching states: **EI**(S_0) or **OA**(S_0). Each of the two scenarios (Fig. 5) involves a sequential transfer of the two protons running through one of the two intermediate forms: the **OI** form (scenario 1) or the **EA** form (scenario 2). Both scenarios differ in the sequence of single proton transfer events (PT). Scenario 1 is initiated by the PT step in which the pyridine skeleton is deprotonated and the H_1 proton is transferred to the carboxylic group – the proton transmitter unit. It is followed by the transfer of the second H_2 proton from the transmitter to pyridine. Scenario 2 describes a different sequence of these events: first, the transmitter is deprotonated and the H_1 proton is transferred to the frame; In the second PT step, the second H_2 proton is transferred toward the transmitter. The reader of publication [H3] can also follow

the evolution of the system separately in the $S_1(\pi\pi^*)$ state and in the $S_1(n\pi^*)$ state visualized by means of the minimum PES for the corresponding excited state.

The analysis of these PES surfaces shows firstly, that in the photophysics of the **3HPA** molecule the reactive state is the excited $n\pi^*$ state – an energetically lower state than the corresponding $\pi\pi^*$ state. It is quite an unusual situation because usually, it is the $\pi\pi^*$ state that is postulated as a reactive state of the ESIPT process in organic molecules. Secondly, we find out that the global minimum of the excited S_1 state is the **EA**($n\pi^*$) form – the same tautomeric form as of the saddle point associated with the energy barrier in the S_0 state. For the **EA**($n\pi^*$) excited-state geometry, i.e. the global minimum of the excited state, the ground state is lying very close to the S_1 state; The energy difference between these states is of ~ 0.37 eV (CC2/cc-pVDZ). Such a result indicates on the presence of a low-lying **CI(S_1/S_0)** near the **EA**($n\pi^*$) minimum, which was confirmed by calculations done with the multi-reference CASSCF method. Because the **EA**($n\pi^*$) form lies near the **CI(S_1/S_0)** region, the population of this form is crucial (i) for the process of nonradiative energy dissipation to the S_0 state – the low-lying $n\pi^*$ reacting state in combination with easy access to the low-energy **CI** point is the reason for the lack of fluorescence of the **3HPA** molecule – as well as (ii) for the photoswitching process between the **EI**(S_0) and **OA**(S_0) forms of the **DPT** photoswitch. The **CI(S_1/S_0)** geometry is a bifurcation point of this process lying nearby the **TS**(S_0) geometry.

Photophysical parameters of the DPT optical switch based on the 3HPA derivatives describing its ground S_0 state and the excited $S_1(n\pi^*)$ state. On one hand, the **DPT** process in the **3HPA** molecule described in publication [H3] showed the potential photoswitching properties of the molecule. On the other hand, it showed the mechanistic problems resulting from the energetics of the PT steps describing the transfer of individual protons to achieve this functionality. The experience and knowledge gained from publication [H2] give us hope for success also in the case of modeling of the **DPT**-class photoswitches based on the **3HPA** molecule.

Therefore, the goal set in the next publication [H4] in the series on photoswitches was to search for such modifications applied to the structure of the model **3HPA** molecule which would induce such change of the PES surfaces, both in the S_0 and S_1 state, so that their shape would be suitable for the functionality of the new system as an optical molecular switch. This task was, therefore, a continuation of the issue undertaken in the publication [H2], but at the

same time a bit more difficult due to the fact that in [H2] the analysis of modifications focused mainly on the excited state.

Discussion on the functionality and properties of the photoswitching molecules led us to formulate a general conclusion that while the both forms of the photoswitch should be energetically isolated in the S_0 state, the easy and preferably barrierless access of the conical intersection **CI(S_1/S_0)** geometry should be ensured after photoexcitation in the area of Franck-Condon of each form of the molecule. In the case of **3HPA**, the **CI(S_1/S_0)** geometry is reached in the $S_1(n\pi^*)$ excited state (Fig. 5). The **CI** geometry resembles the geometry of the **EA**($n\pi^*$) minimum and this form is responsible for the process of rapid internal conversion from the S_1 to S_0 state due to the small difference in energy between the $S_1(n\pi^*)$ and S_0 states. This process may happen under the condition of the lack or existence of a low-energy barrier in the $S_1(n\pi^*)$ state separating the **EA**($n\pi^*$) form from both light-induced tautomeric forms. Scenario 2 was proven to be the dominant process in the photoswitching mechanism of the **3HPA** molecule (Fig. 5).

Summary. Desired photophysical parameters for the S_0 state. In the context of the molecular switch, the both forms of the molecule should have similar relative energies and a high energy-barrier separating them. Therefore, my efforts related to the modeling of the **DPT** photoswitch were aimed at stabilizing the both forms relative to each other while maintaining a sufficiently high energy barrier in the S_0 state. An additional difficulty was to maintain photochromism of the system, i.e. a sufficiently large difference between the vertical excitation energies (λ_e for **EI**(S_0) and λ_p for **OA**(S_0)) to the strongly absorbing $\pi\pi^*$ states in the absorption spectrum of the both forms. All the photophysical parameters of the optical switch based on the **DPT** process are presented in Fig. 5.

Requirements for the S_1 state are different than for the S_0 state. The main goal here for the system is to reach the **CI(S_1/S_0)** region as easy as possible, the best in a barrierless manner. In this context, the access of the **EA**($n\pi^*$) form after photoexcitation of both the **EI**(S_0) and **OA**(S_0) forms is crucial for ensuring the reversibility of the photoswitching process. Thus, one of the main goals set in publication [H4] on modeling the PES surface of the S_1 state was to model a photoswitch molecule in which the energy barrier in the $S_1(n\pi^*)$ state would be significantly reduced for the **OA** → **EA** photoswitching process in comparison to the barrier for the parent **3HPA** molecule (+ ~0.43 eV).

Search for suitable structural modifications of the 3HPA molecule in order to achieve photo-switching functionality. The purpose of this search was to model a new molecule with photoswitching features for which the photoswitching process would be based on the described **DPT** mechanism. I wanted to show that appropriate modifications of the **3HPA** structure will enable the reversible **DPT** process in the S_1 state and inhibit the thermal back reaction in the S_0 state. Changes in the photophysical parameters induced by (a) the substituent effect applied to the **3HPA** frame, (b) insertion of additional nitrogen atom into the **3HPA** frame (the idea for this molecular modification type resulted from the recent publication[27]), and (c) increase in the frame size by fusing an additional benzene ring to the pyridine ring are discussed.

One of the most important observations is the lack of influence of the methyl, $–CH_3$, group on the potential energy landscape of the S_0 and S_1 states which coincides with the same conclusion in publication [H2]. However, in the case of the $–NH_2$ group – a strong electron donating one – we noticed a strong dependence of the substitution effect on the substitution position of this group. The substitution of the $–NH_2$ group at the C_4 position results in the reduction of the energy barrier δ in the $S_1(n\pi^*)$ state as well as in the fact that the reaction in the $S_1(n\pi^*)$ state becomes more exoenergetic and thus the **CI** geometry becomes more easily populated. The additivity of various types of structural modifications was also tested including the effect of simultaneous substitution of electron-donating and electron-accepting groups – the so-called the push-and-pull effect.

An important conclusion of this publication is the observation that while it was much easier to improve the photophysical energetic parameters of the S_0 state, at the same time it was much more difficult to maintain the excitation selectivity condition. It is important for the photoswitch that each tautomeric form, here **EI**(S_0) and **OA**(S_0), has its own spectral absorption window that could transform one form into another upon the influence of light.
What was also investigated was the influence of these modifications on the defined photoswitching parameters of the given molecule as well as on the size of the energy gap between the different types of excited states: $S_1(n\pi^*)$ and $S_1(\pi\pi^*)$, and therefore, on the ordering of these states.

Finally, it was shown in publication [H4] that the various methods of structure modification applied together give a qualitatively additive effect. This observation was consistent with the conclusion of Nenov and Vivie-Riedle based on the study of polyene photoreactivity in the context of access of the **CI(S_1/S_0)** region in the photoprocess.[59] Each modeling step

improving the switching behavior of the new structure was illustrated by a corresponding energy diagram showing Scenario 2 of the **DPT** mechanism in which the photophysical parameters requiring correction were diagnosed (see Figs. 2, 3 and 4 in publication [H4] and compare with the diagram for **3HPA** – Fig. 1 in [H4]). In addition, energy diagrams according to the both scenarios for selected modifications have been included in the Supplementary Information (SI) in publication [H4].

Summary of publications H3 and H4. The search for appropriate types of structural modifications in the **DPT**-based switching mechanism occurred to be more demanding compared to the **TPT** mechanism because they required improving the PES surface landscape of both ground and the excited states at the same time, and additionally required fulfilling the excitation selectivity condition. Regarding tuning of the shape of the PES landscape of the excited state by means of the substituent effect, in both the photoswitching mechanisms: **TPT** and **DPT**, I noticed some common features: e.g. (i) π-electron-donating substitution can have a very large impact on the shape of this landscape. Moreover, this effect can be varied depending on the position of the substitution. (ii) The methyl groups practically do not change the excited state potential energy landscape, unless they constitute a steric blockade. An important phenomenological difference is a fact that in the **TPT** mechanism the reactive state was $S_1(\pi\pi^*)$, while it was the $S_1(n\pi^*)$ state dominating in the **DPT** mechanism. Additionally, it should be noted, that the system in which the ESIPT process takes place in the $S_1(n\pi^*)$ state is rare among the ESIPT systems, in literature.

2.4. Model of a ferroelectric field switch functioning as an electric field sensor (publication H5).

Motivation to undertake research. In publication [H3] the mechanism of double proton transfer (**DPT**) in the ground S_0 state of the **3HPA** molecule and in its two excited states: $S_1'(\pi\pi^*)$ and $S_1''(n\pi^*)$ was studied. The shown differences in the PES surface landscape of these states indicate significant differences in the mechanism of the **DPT** process in the **3HPA** molecule occurring in the S_0 state and after electron excitation. Similarly in publication [H5], we decided to examine the changes of the **DPT** mechanism which could be induced by an electric field applied to the molecule as a function of the fields amplitude and direction. Additionally, taking advantage of the fact that the studied process takes place in the S_0 state, we decided to support the results of the static calculations by using the "on the fly" molecular dynamics simulations. Apart from giving the illustration of the **DPT** mechanism in the

presence of an electric field, it allowed us to estimate the time-scale of the studied **DPT** process.

Discussion (publication H5). In publication [H5] a model of a ferroelectric molecular switch is presented which reversible switching mechanism is controlled by the magnitude and direction of the applied external electric field. The studied (2Z)-1-(6-((Z)-2-hydroxy-2-phenylvinyl)pyridin-3-yl)-2-(pyridin-2(1H)-ylidene)ethanone molecule (**DSA**) (Fig. 6), a derivative of the aromatic Schiff base, has two intramolecular hydrogen bonds spanned

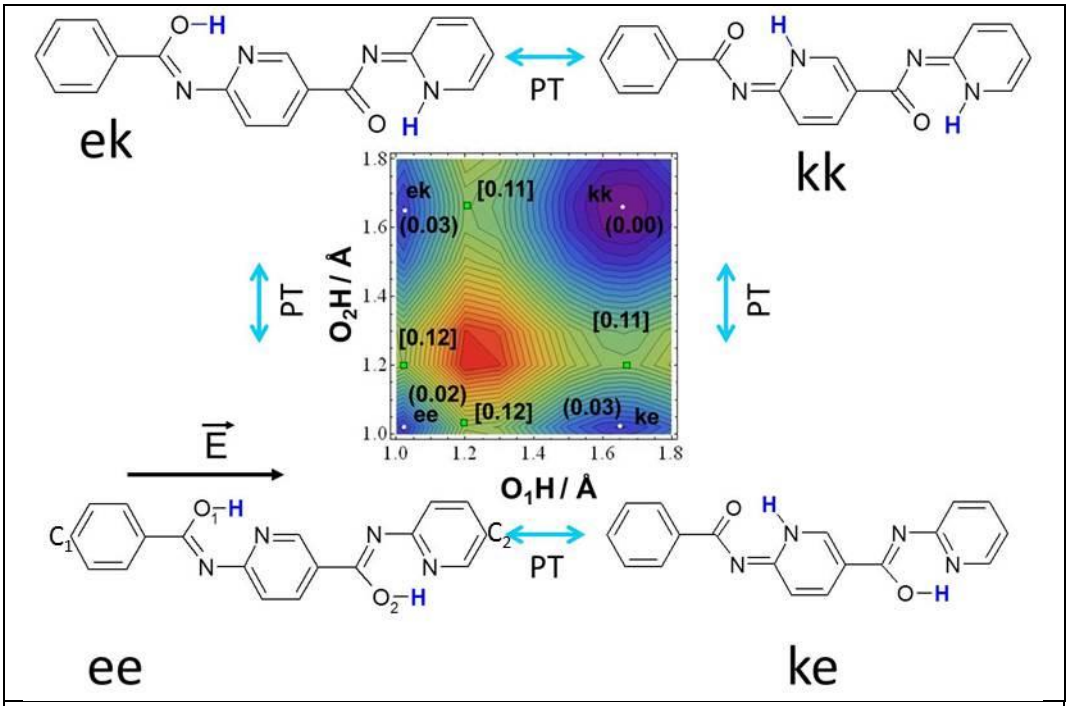


Fig. 6. Four tautomeric forms of the **DSA** molecule. Enumeration of atoms

between the oxygen and nitrogen atoms: O_1-H$\circ\circ\circ N_1$ and O_2-H$\circ\circ\circ N_2$. The static calculations using the DFT method for the ground S_0 state for the **DSA** molecule showed that the system has four stable tautomeric forms: **ee**, **ek**, **ke**, and **kk**, which in conditions without an applied electric field should coexist in thermal equilibrium, because these forms are separated by low-energy barriers ~+0.1 eV. The shape of the S_0-state potential energy surface (PES) shows that the process of transfer of two protons along the main axis of the molecule should be an asynchronous process, comprising of the two separate, consecutive transfer processes of a single proton, because energy barriers separating the single proton transfer processes occurred to be lower than the barrier to the synchronous transfer of the two protons – along the S_0-PES diagonal (**ee** – **kk**). When the electric field is switched on and applied along the main axis of the molecule defined by the C_1-C_2 bond (see Figs. 3, S2, S3 in SI [H5]), both protons are transferred along the hydrogen bond bridges from the **ee** form to the **kk** form at the positive

field values (E > 0.107 a.u.). With this value of the field, the **kk** form is the only stable form of the system. However, when the direction of the applied field is changed and its magnitude is decreased down to negative values (E < -0.105 a.u.), the **kk** form becomes completely destabilized and the both protons are transferred back to the **ee** form – the only stable form of the system at this direction and the magnitude of the applied electric field.

This process is possible because the **DSA** molecule is ferroelectric – its two tautomeric forms: **ee** and **kk**, are characterized by the opposite sign of the electric dipole moment, μ_g (-2.8 Debye, for the **ee** form and +7.8 Debye for the **kk** form, determined using the B3LYP/cc-pVDZ method). The applied electric field interacts with the dipole moment of the molecule. Except for determining the critical values of the electric field at which the barrierless transfer of both protons takes place, the main aim of publication [H5] was to study the mechanism of the double proton transfer in the S_0 state (S_0-**DPT**) in the **DSA** molecule as a function of the magnitude of the applied electric field and afterwards, to propose an appropriate functionality for this molecule. The results of static calculations, illustrated by properly constructed PES surfaces as a function of the magnitude of an applied electric field, showed that the **DPT** mechanism changes its character from a two-step reaction, in a situation with no field applied, to a single-step, when higher magnitude electric field is applied. Whereas in conditions without an applied field, E = 0, the molecule is in the thermodynamic equilibrium of the four coexisting energetically equivalent tautomeric forms, shown in Fig. 6. The energy-barrier visible along the **ee-kk** diagonal on the S_0-PES surface (seen in Fig. 6) is gradually disappearing when the magnitude of the electric field applied is systematically increased (see Figs in SI [H5]). Thanks to this, the synchronous transfer of the two protons becomes possible.

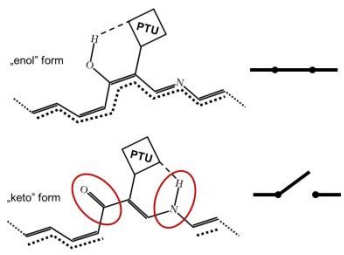
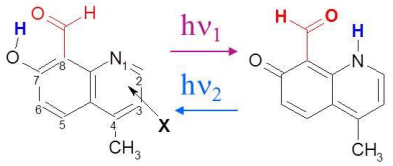
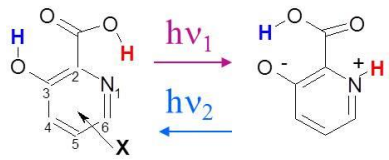
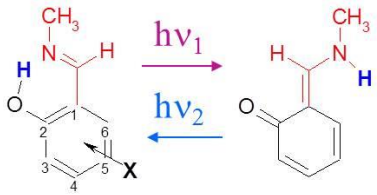
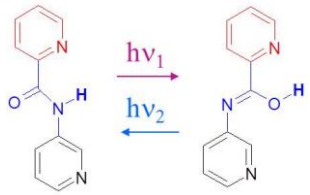
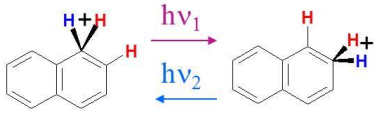
Additionally, the "*on-the-fly*" molecular dynamics simulations for the **DSA** molecule performed in the presence of the electric field and without the field confirmed the conclusions drawn from the static calculations. They showed that the mechanism of the double proton transfer is changed from the asynchronous reaction, with the field switched off, to mixed – synchronous/asynchronous process – with the electric field switched on. The effect depends both on (i) the magnitude of the electric field applied and on (ii) its polarization. The critical field values at which both protons are transferred in a barrierless manner from the **ee** to **kk** form (with positive field values, E> 0.107 a.u.) and when both protons are transferred back from the **kk** to **ee** form (at negative field values, E <-0.105 a.u.) were determined using static calculations.

Another achievement of publication [H5] was to propose molecular functionality for the **DSA** molecule which should be related to the studied **DPT** mechanism. While the tautomeric forms of the **DSA** molecule absorb strongly in the energy range 3.5 - 4.5 eV, and their absorption bands overlap, the situation changes when we apply a strong electric field to the molecule. Depending on the amplitude and direction of the electric field, the absorption spectrum changes when the **ee** form dominates (E < -0.105 a.u.) and when dominates the **kk** form (E> +0.107 a.u.), see Fig. S11, publication [H5].

2.5. Summary.

In summary, publications [H1-H5] constitute a monothematic series of studies devoted to theoretical optimization of the properties of the molecular proton switch, which can be controlled by two types of stimuli – optically – by UV-irradiation of the molecule, or by appropriately applied to the molecule an external electric field. In my research, I focused on searching for new mechanisms and maybe even more on designing appropriate molecules that could meet the appropriate requirements set by a given type of photoswitching mechanism. The photoswitching systems studied by me, which photophysics is based on the transfer of the proton in the excited state, S_1, are gathered in Table 5. The main trend of studies on molecular photoswitches was related to the **TPT** mechanism to which the most publications were devoted: [H2, P2, P5, P6]. A similar mechanism, also based on the ESIPT process assisted by the proton crane rotation was undertaken by Joanna Jankowska as part of her PhD thesis [P3, P7]. Finally, in addition to the **TPT** and **DPT** mechanisms described in this Summary, we should mention an interesting **Hula-Twist** mechanism which we used in conjunction with the ESIPT process as one of the types of photoswitching mechanisms described in [P8, O1, N1].

Table 5. The photoswitching mechanisms based on ESIPT phenomenon studied by me.

	The transfer of the proton between the two remote oxygen and nitrogen atoms switches the two forms of the conducting polimer: „enol" and „keto" differing by voltaic characteristic, publication [P1]
	The **TPT**-type photoswitch based on the ESIPT process assisted by the twist of the proton crane (*proton-craning Twist-assisted ESIPT*), publications: [H2, P2, P5, P6]
	The **DPT**-type photoswitch based on the double ESIPT process mediated by the proton transmitter unit. (*proton-transmitter mediated double ESIPT*), publications: [H3, H4]
	The **TPT**-type photoswitch based on the ESIPT process assisted by the TWIST of the proton crane publications: [P3, P7]
	The **Hula-Twist**-type photoswitch transferring the proton between the two oxygen and nitrogen atoms assisted by the "bicycle pedal" motion of the molecule, publications: [P8, O1, N1]
	The photoswitch molecule in which the excess proton is transferred between the two neighboring carbon atoms in the protonated naphthalene molecule, publication [P4]

2.6. My plans for scientific future.

During one of the international conferences I attended, I established a scientific cooperation with Dr. Gotard Burdziński from the University of Adam Mickiewicz in Poznan. Dr. Burdziński's scientific interests are connected with the photophysics of natural dyes present in plants. His experimental techniques include time-resolved infrared and electron spectroscopy. In combination with my experience in the field of studying the processes undergoing in the excited-states by means of *ab initio* methods, we try to explain the fast excited-state

deactivation processes in the betaxanthin molecules: miraxanthin V [M14, App. 5] and miraxanthin I (publication in preparation stage). The process is important from the point of view of protection of plants against the excessive exposure on sunlight. Additionally, our joint research focuses on the photophysics of photochromic molecules, such as 3H-naphthopyran. Currently, we are jointly implementing a scientific project on this subject, whose Leader is Dr. Burdziński, and I am responsible for performing *ab initio* calculations.

Experience and knowledge gained from the publications included in the habilitation thesis: [H2] and [H4], in particular concerning the methodology in structural modification aimed at searching for the compounds with desirable photophysical properties, I hope to use in future research and searching for new molecules with different photophysical properties and new functionalities.

The quantum chemistry methods available today make it possible to carry out calculations in both the ground and in the electronically excited states. Thanks to this, we can predict photophysical properties of molecules, such as absorption from the S_0 state and emission from the S_1 state. So far, the calculations for molecules placed in an external electric field are limited to the ground state. The programs enabling the calculations of the excited state properties of the molecules placed in the electric field will be available soon. Such a tool will make it possible to design, by means of *ab initio* methods, new devices – molecular machines – using the optical excitation and electric field stimulation simultaneously, or alternatively. This will allow us to design additional devices, such as phototransistors or electric filed assisted photoswitches.

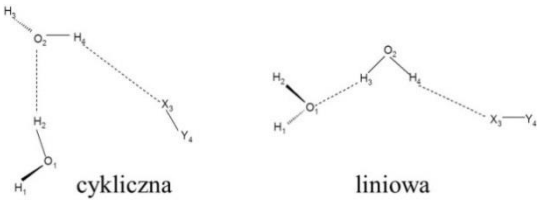
One could say: "unite the switches". Recently, a four-stable photoswitch was presented which combine several different switching mechanisms: two induced by light – one based on the ESIPT process and the other one on the ring opening reaction[60] – and one based on chemical complexation with metal. The operation of this photoswitch was confirmed experimentally.[60] Thus, it seems that the research on photoswitches based on the ESIPT process still have a future and will be continued by me, while there appear more and more new photoswitch molecules, e.g. based on the **TPT** mechanism[45, 46] that have been discussed here. In contrast, there appear also completely new photoswitching systems and new or related ESIPT-type mechanisms, which are in a way a continuation of my research in the field of the molecular photoswitches. In another perspective, one may study the substituent effect used to model the processes in the excited state – for example, absorption or emission.[61, 62]

3. DISCUSSION OF OTHER SCIENTIFIC ACHIEVEMENTS

3.1. Description of the research not contributing directly to the habilitation theses

3.1.1. Research conducted prior to obtaining PhD in chemistry

During my master's and doctoral studies at the Faculty of Chemistry at the University of Warsaw, I specialized in quantum-chemical calculations of the weakly bound molecular clusters. As part of my master's thesis, I investigated the nature of interactions in the carbon monoxide dimer. The results of these studies were published as the first two publications of my co-authorship [D1 and D2, App. 5]. It wasn't an easy task since it is difficult to correctly reproduce the size and sign of the dipole moment of the carbon monoxide molecule. Both my master's and doctoral thesis were done under the supervision of Prof. Joanna Sadlej at the Faculty of Chemistry at the University of Warsaw. During my doctorate studies, in the same Laboratory, I continued research on weak interactions in molecular clusters. I dealt with the study of three-body non-additive interactions in the intermolecular trimers consisting of the water dimer complex interacting with a diatomic molecule, such as CO, N_2 or hydrogen halides, HX. An exceptionally interesting conclusion from these studies was the fact that obtaining a stabilizing energy effect, manifested by a negative value of non-additive contribution in the interaction energy, $\Delta E_{int,\ NA}$, depends on the most stable, cyclic arrangement of the three molecules in the figure resembling an equilateral triangle in which all three dimers forming the trimer interact effectively (see Fig. 7). The linear arrangement of



$E_{int} < 0.0$ $E_{int} < 0.0$

$E_{int,\ NA} < 0.0$ $E_{int,\ NA} > 0.0$

Fig. 7. Stable forms of the studied trimers: $(H_2O)_2 \circ\circ\circ$ XY, XY=N_2, BF, CO, H_2, HCl, HF, HBr, ClF. Even though, the interaction energy of the trimer, E_{int}, is negative, its trhree-body non-additive contribution - $E_{int,\ NA}$, may be either

the molecules is not the most favorable for the whole trimer, which is reflected by the positive value of $\Delta E_{int,\ NA}$. Such observation made on molecules is an example of a synergistic effect known from various fields of science, including humanities. The results of studies on the trimers were published in three publications: [D3-D5, App. 5]. In the series of these publications, I showed that boththe structure, the shift of appropriate bands in the IR spectrum and the height of proton tunneling barriers depend on the electrical properties of the XY diatomic molecule interacting with the water dimer.

During my doctoral studies, I completed a three-month pre-doctoral internship at the Jackson State University, in Jackson, USA. The results obtained during this internship were presented in publication [M1].

3.1.2. Research conducted after obtaining PhD in chemistry

After defending my doctoral thesis, I took a postdoctoral internship at the Department of Chemistry at the Oakland University in Rochester, USA. The research concerned the weak interactions of the transition metal atoms, or their cations, with the helium atom. The results of these studies have been published in two publications: [M2, M3 (M3a)], including one in *Phys. Rev. Lett*. After returning from the USA, I went to Germany to take a postdoctoral position at the Faculty of Chemistry at the Stuttgart University, where I studied, by means of the theoretical methods, the model of the active center of the hemocyanin protein, the molecule responsible for oxygen transport in invertebrates animals. The research was published [M4]. Both postdoctoral positions allowed me to broaden my knowledge of theoretical methods and learn how to use the MOLPRO calculation software package.

So far my research was focused solely on the weakly interacting molecular complexes bound by van der Waals forces, such as dimers - composed of the two atoms, e.g. a transition metal, or its cation, interacting with the helium atom [M2, M3, M3a] or a chlorine anion (or atom) interacting with the acetonitrile molecule (or its dimer) [M1] - in the electronic ground-state of these complexes.

A definite change of my research topics awaited me in my new workplace. After foreign internships, I was employed as a post-dock at the Institute of Physics of the Polish Academy of Sciences, where I work until today. Thanks to many years of cooperation with Prof. Andrzej Sobolewski, who introduced me to the theoretical studies of molecular photophysics, I learned theoretical methods of quantum chemistry that are dedicated to describe the properties of molecules in their excited states.

Mechanisms of the fluorescence quenching

The experience and scientific achievement derived from the publications described in this Summary, allowed me to build up tools which I use today to study other molecular systems. As an example of such work is the study of the photophysics of miraxanthin V [M14]. Together with Dr. Gotard Burdziński we indicated the reasons for the short fluorescence decay time for this molecule (Fig. 8) using quantum mechanical calculations for the excited state and time-resolved electron spectroscopy.

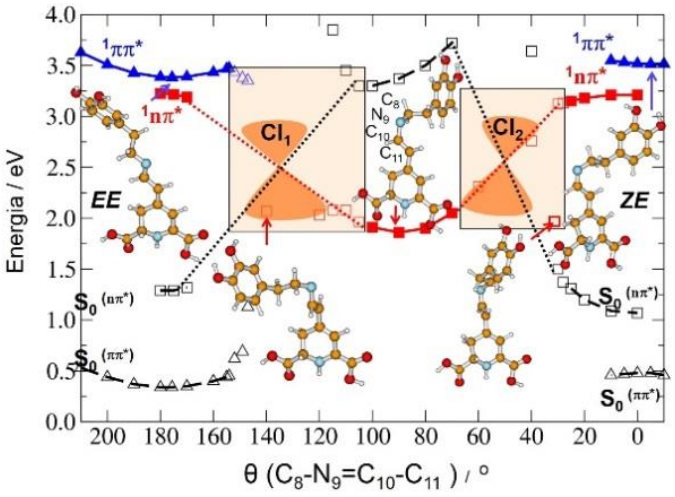


Fig. 8. Photophysics of miraxanthin V, a natural dye existing in yellow *Mirabilis jalapa* [M14]. The shape of the potential energy profiles in the miraxanthin V molecule in its ground electronic state, S_0, and in the electronically-excited states: $^1\pi\pi^*$ and $^1n\pi^*$, determined at the MP2(S_0) and ADC(2)/def-SV(P) (S_1) level indicates on fast deactivation pathway leading through the **CI(S_1/S_0)** region.

The key to indicating these reasons was the analysis of the geometrical parameters changes which undergo in the dye molecule upon the electron excitation. This analysis is an example of applying the knowledge drawn from the publications covered by the habilitation achievement [H1]. A publication on the photophysics of this dye derivative – miraxanthin I – is being prepared. Another example of a system that does not emit light is a protonated benzene. The mechanism of the excited-state deactivation process for this system was examined by me together with an experimental research group and described in publication [M6]. The theoretical achievement of this publication is to propose a stair-case mechanism of the excited-state deactivation process. It is based on numerous conical intersections between the above-lying excited-state potential energy surfaces (PES) with the PESes of lower lying electronic states. In the theoretical analysis, it was much helpful that each of the four lowest excited states belonged to a different irreducible representation of the C_{2v} symmetry group, thanks to which the geometry of each state could be optimized independently of the others.

Modeling the molecules to modulate their different physical properties.

Another example of the application of knowledge derived from publications [H1-H4] is a skillful modification of the structure of a given molecule in order to obtain its proper (photo-) physical properties such as:

- emissive properties of the molecules.

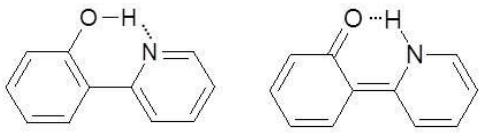
In publication [M9], the molecules differing in the number of triple bonds in the polyyne chain, which acted as a separator between the two benzene rings in the molecule, were studied by means of the spectroscopic and theoretical methods. The achievement of this work was to explain, on the basis of theoretical calculations, the lack of emission for a molecule with four

triple bonds, in which the dark state was the lowest excited state. On the other hand, the molecule with a single triple bond in the chain emitted fluorescence, because the lowest excited state in this molecule was the state with an allowed radial transition to the S_0 state.

In turn, the main purpose of publication [M15] was to synthesize and study the emission properties of the *dipyrrolonaphthyridinediones* (DPND) molecule. The effect of substitution with an electron donating diethylamine group, $–MEt_2$, was demonstrated in this study to reduce the emission energy of the molecule. New molecules with interesting emission properties for further synthesis have also been proposed.

- current-voltage characteristic of the molecules.

In publications [M12] and [M13], the **2PPy** molecule (Fig. 9) was studied. Its chemical structure is built of two subunit molecules: phenol and pyridine, that are bound with each other with a covalent bond. In its structure there is also an intra-molecular hydrogen bond – indicated in Fig. 9 – which allows the coexistence of the molecule in two tautomeric forms: enol and keto. These two forms differ in their voltage-current characteristics. Applying an external electric field with large enough magnitude and direction results in the populations of a given form of the molecule. In publication [M13], various chemical groups have been proposed acting as molecular contacts of the molecule with the gold electrodes applied to it.



enol **keto**

Fig. 9. Two tautomeric forms of the **2PPy** molecule with the intramolecular hydrogen bond indicated by a dashed line. Publications [M12,M13].

Photoisomerization processes

Most of the publications from the period after obtaining the doctoral degree in the field of chemistry concerned various mechanisms of photoisomerization processes, among which one should distinguish *cis*/*trans* photoisomerization [M14, M8]. The sub-class of the studied photoisomerization processes is the enol/keto [P1-P3, P5-P8, M5, M10 and H2-H4] and imine/amine phototautomerism [H1, H3, H4]. The mechanism of the transferring the proton between the neighboring carbon atoms in the protonated naphthalene molecule was also investigated [P4], see Table 5. A very interesting mechanism of the enol/keto phototautomerism is shown in publication [M5], namely the photoinduced transfer of the proton of the dissociative-associative type, PIDA (Photo-Induced Dissociation-Association, Fig. 10). The essential role of the excited $\pi\sigma^*$ state has been here demonstrated, on the

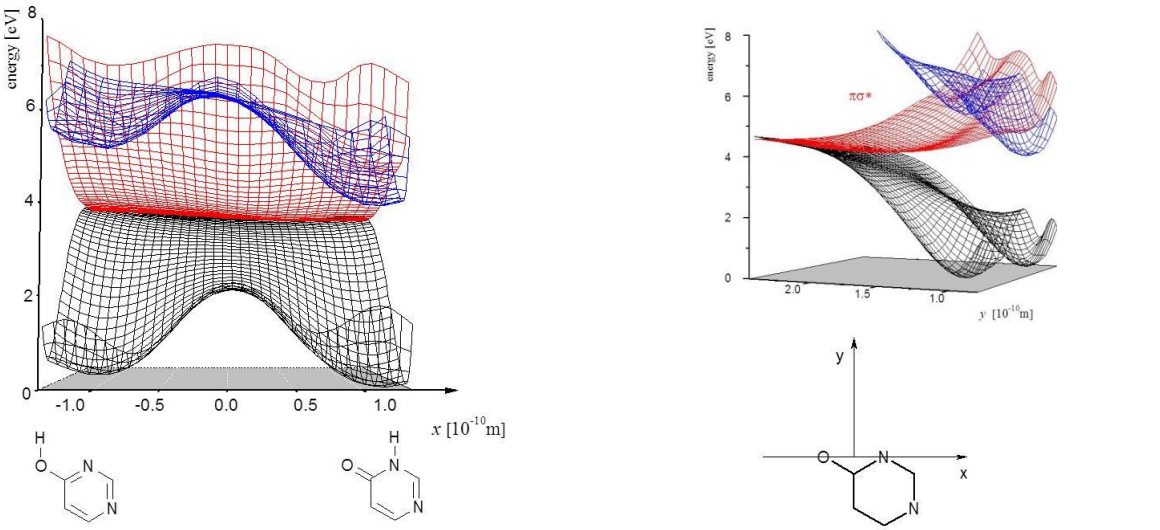


Fig.10. Photo-Induced Dissociation-Association mechanism of the proton transfer, PIDA (publication [M5]). Potential energy surfaces in the S_0 state (black), in the locally-excited state, $^1\pi\pi^*$ (blue) and dissociative **πσ*** (red) for the 4-hydroxy-pirymidine molecule. View along the proton transfer (x) and its dissociation (y) coordinate.

example of the 4-hydroxy-pyrimidine molecule, which mediates in the initial light-induced proton departure from the molecule (photodissociation) to the distance of ~2Å where the system reaches the conical intersection **CI(S_1/S_0)** seam. There, the strong non-adiabatic interactions cause the transition of the system to the ground state which initiates the proton return process. Already in the S_0 state, the proton returns toward the molecule and associates with it (association) with a covalent bond. Association of a proton may occur in a different (than initial) place, hence it is tautomerization.

Publications made in cooperation with the experimental research groups.

In my scientific output apart from purely theoretical publications, there are many such that were published in a collaboration with experimental research groups. Theoretical calculations in these studies have often been helpful in determination of the proper form of the experimentally observed molecule, either by means of absorption or light emission, or simultaneously by means of both methods: [M10, M11, M14, M15, P4, P5, P6, P8]. Quite often, calculations required the determination of an energy-barrier in the excited state in order to determine the correct molecular form emitting fluorescence. In this context, I would distinguish publication [M10] in which, on the example of the 2-carboxy-inodole molecule, the process of the proton transfer in the excited state from the carboxyl group to the indole nitrogen was investigated directly through the intramolecular hydrogen bond and with the assistance of the water molecule in the so-called relay fashion.

Acknowledgments

Here I would like to say thank you to all my co-authors, without which some of the publications would not have been created and for the friendly atmosphere at work. Special thanks to:

- Prof. Andrzej Sobolewski for introducing me in the subject of the photophysics of molecules and for sharing knowledge about their electronically excited states.
- Dr. Jacek Nowacki, for the synthesis of compounds with the character of the **TPT** class photoswitches, the derivatives of 7-hydroxyquinoline. What a pity he is not with us anymore.
- Dr. Joanna Jankowska, and above all, Dr. Gotard Burdziński for countless discussions and deeply motivated questions for further work.

3.1.3. Bibliometric summary of scientific publications

Today, I am the author of 33 scientific publications (5H + 8P + 15M + 5D) all of which are published in the Thompson Reuters high-IF journals (28 publications after obtaining the doctoral degree). My Hirsh index is 13, according to the "Web of Science" database, the first two publications, [D1] and [D2], published together with prof. Joanna Sadlej, are co-authored by me as Michał Rode (without the initial "F"). Publication [M3a] is only a correction of publication [M3].

Number of publications (published in journals listed in the Web of Science database: **33** (a full list in Appendix No. 5)
Number of publications (after obtaining PhD in chemistry): **28**
Number of book chapters: 1
Total impact factor of these publications calculated according to the Web of Science, as in the year published: **101,364** (3,072/publ.)
Number of citations (without self citations) according to the Web of Science: **648** (581)
Hirsh index according to the Web of Science: **13**

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