Photoinduced processes in molecular systems with proton and electron transfer of potential applications in optical memories and solar cells, studied by time-resolved optical spectroscopy methods.

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1. Personal data

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2. Education and scientific degrees

D. Sc.(Physics)	2003	Adam Mickiewicz University in Poznan, Faculty of Physics Title: "The analysis of linear and nonlinear physical processes in the femtosecond two-pulse spectroscopy" Supervisor: Prof. Dr. hab. Ryszard Naskręcki
M. Sc.(Physics)	1999	Adam Mickiewicz University in Poznan, Faculty of Physics Title: "A system for transient absorption measurements to a femtosecond resolution; preliminary and testing measurements" Supervisor: Prof. Dr. hab. Franciszek Kaczmarek

3. Information about past occupation in scientific units

since 2008: adjunct in Quantum Electronics Division, Faculty of Physics,
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2003-2008: adjunct in Center for Ultrafast Laser Spectroscopy,
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4. Presentation of research achievement making basis for habilitation degree procedure

In terms of the Act of 14 March 2003, art. 16, item 2, on the scientific degrees and scientific title and the degrees and titles in the arts (Journal of Laws, No 65, item 595 with amendments) the scientific achievement making basis for habilitation degree procedure is the research work reported in the series of 11 papers under a general title:

Photoinduced processes in molecular systems with proton and electron transfer of potential applications in optical memories and solar cells, studied by time-resolved optical spectroscopy methods.

4.1. The list of monothematic papers making basis for habilitation degree procedure

Number	Title and authors	Impact Factor (according to the year of publication)
H1	M. Ziółek, G. Burdziński, K. Filipczak, J. Karolczak, and A. Maciejewski, *Spectroscopic and photophysical studies of the hydroquinone family of photochromic Schiff bases analyzed over a 17-orders-of-magnitude time scale,* Phys. Chem. Chem. Phys., **10** (2008) 1304-1318.	4.064
H2	M. Ziółek, K. Filipczak, A. Maciejewski, *Spectroscopic and photophysical properties of salicylaldehyde azine (SAA) as a photochromic Schiff base suitable for heterogeneous studies,* Chem. Phys. Lett. **464** (2008) 181-186.	2.169
H3	M. Ziółek, I. Sobczak, *Photochromism and hydrolysis of aromatic Schiff base N,N'-bis(salicylidene)-p-phenylenediamine (BSP) studied in heterogeneous environments,* J. Incl. Phenom. Macrocycl. Chem., **63** (2009) 211-218.	1.165
H4	M. Ziółek, G. Burdziński, J. Karolczak, *Influence of Intermolecular Hydrogen Bonding on the Photochromic Cycle of the Aromatic Schiff Base N,N'-Bis(salicylidene)-p-phenylenediamine in Solution,* J. Phys. Chem. A, **113** (2009) 2854-2864.	2.899

H5	K. Filipczak, J. Karolczak, M. Ziółek, *Temperature influence on deactivation paths and tautomeric equilibrium of some photochromic Schiff bases studied by time-resolved and stationary spectroscopy,* Photochem. Photobiol. Sci., **8** (2009) 1603-1610.	2.708
H6	M. Ziółek, M. Gil, J. A. Organero, A. Douhal, *What is the difference between the dynamics of anion- and keto-type of photochromic salicylaldehyde azine?* Phys. Chem. Chem. Phys. **12** (2010) 2107-2115.	3.454
H7	M. Ziółek , X. Yang, L. Sun, A. Douhal, *Interrogating the ultrafast dynamics of an efficient dye for sunlight conversion* Phys. Chem. Chem. Phys., **12** (2010) 8098-8107.	3.454
H8	M. Ziółek, I. Tacchini, M. T. Martínez, X. Yang, L. Sun, A. Douhal, *Photo-induced electron transfer study of an organic dye anchored on the surfaces of TiO2 nanotubes and nanoparticles,* Phys. Chem. Chem. Phys., **13** (2011) 4032-4044.	3.573
H9	M. Ziółek, C. Martín, M. T. Navarro, H. Garcia, A. Douhal, *Confined Photodynamics of an Organic Dye for Solar Cells Encapsulated in Titanium-Doped Mesoporous Molecular Materials,* J. Phys. Chem. C **115** (2011) 8858--8867.	4.805
H10	M. Ziółek, B. Cohen, X. Yang, L. Sun, M. Paulose, O. K. Varghese, C. A. Grimes, A. Douhal, *Femtosecond to millisecond studies of electron transfer processes in a donor–(π-spacer)–acceptor series of organic dyes for solar cells interacting with titania nanoparticles and ordered nanotube array films,* Phys. Chem. Chem. Phys., **14** (2012) 2816-2831.	3.573*
H11	M. Ziółek, G. Burdziński, A. Douhal, *Long-living Structures of Photochromic Salicylaldehyde Azine: Polarity and Viscosity Effects from Nanoseconds to Hours* Photochem. Photobiol. Sci., **11** (2012) 1389-1400.	2.584*

* - Impact Factor from 2011

Total Impact Factor (IF) of papers [H1] – [H11]: 34.448

Mean Impact Factor: 3.132

4.2. The aim of the research work described in the papers H1-H 11 and the results achieved and indications of their possible applications

A) Introduction

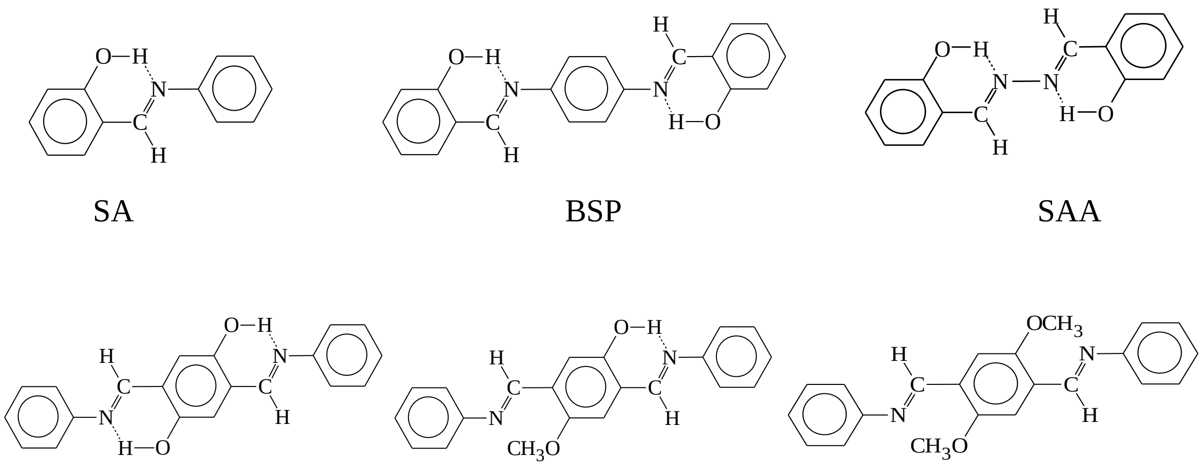
The general aim of the research presented in the series of 11 papers [H1-H11] was investigation of molecular systems that could be used in optical memories and solar cell by the methods of optical spectroscopy and in particular time-resolved spectroscopy. The molecular systems studied can be divided in two groups. The first group includes the photochromic aromatic Schiff bases. The results obtained for these compounds are described in [H1-6] and [H11] and permitted determination of the rate and yield of formation of the species showing completely different optical (absorption) properties than the original species and estimation of the lifetime of such a photochromic species. From the point of view of optical memories, the yield of the photochromic species should be as high as possible and its lifetime should be as long as possible, and simultaneously it should be possible to be effectively converted into the original species under the effect of light. The second group of molecular systems comprises the compounds from the family of triphenylamines that can be used in the dye sensitized solar cells, DSSC. The interaction of these molecules with titanium oxide nanoparticles permits the injection of an electron from the photo-excited dye into the network of nanoparticles, which is fundamental for charge separation in the solar cell. The research work reported in [H7]-[H10] permitted determination of the rate of charge injection, the rate of the competing processes and quantum yield of electron transfer.

A common feature of these two classes of compounds is the occurrence of a very fast intramolecular transfer of proton or electron triggered by light absorption, which initiates further processes of formation of a photochromic species or generation of current in the solar cell. In the Schiff bases a proton is transferred within the intramolecular hydrogen bond, while in the family of triphenylamines an electron is transferred from a donor to an acceptor group. The results reported in [H1-H11] have been obtained by the same methods of which the most important was the time-resolved optical spectroscopy employing the laser pulses in a very wide range of time - from femto- to milliseconds.

In the following part of this presentation when referring to the work, results and conclusions published in the series of papers labelled with H and listed in 4.1, I will use the first person singular (as expressed in the declarations of co-authors my contribution to them was at least 60%). When referring to the work, results and conclusions of the other papers I co-authored (often to a high degree) but outside the above list, labelled with a letter P in the list of all papers I co-authored, I will use the first person plural.

B) Schiff bases and photochromism

The structural formulae of Schiff bases I chose to study are presented in Fig. 1. These compounds have intramolecular hydrogen bond between the hydrogen from a hydroxyl group (-O-H) and the nitrogen N from an imine group, except for BPHMe$_2$.



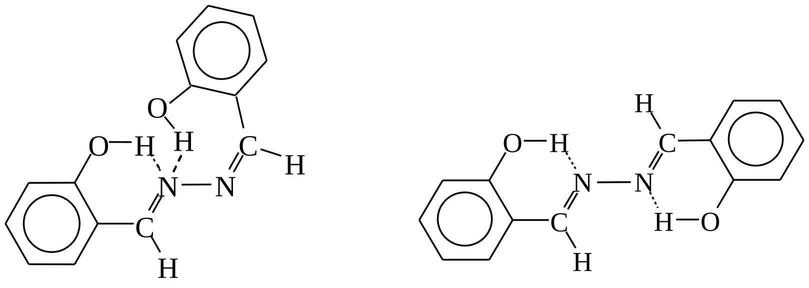
SA BSP SAA

BPH BPHMe BPHMe$_2$

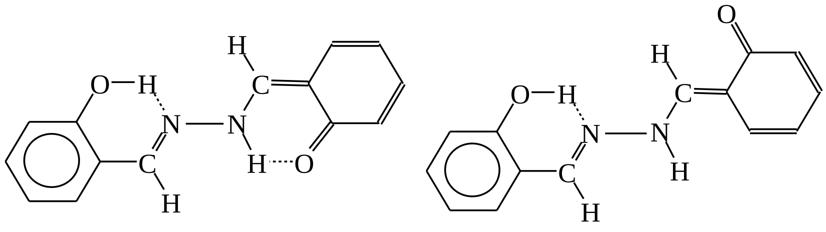
Fig. 1. Structures of the aromatic Schiff bases studied.

The model Schiff base from this group is salicylideneaniline (SA), whose promising photochromic properties have been known from a few ten years [1]. I was mostly concerned with its two symmetric derivatives salicylaldehyde azine (SAA) and *N*,*N′*-bis(salicylidene)-*p*-phenylenediamine (BSP) and a dimethoxy BSP derivative as a reference compound (BSPMe$_2$). Their symmetry (two hydrogen bonds) extends their potential use by formation of complexes and nanostructures [2,3] in which the additivity of many parameters in the ground state is employed. In contrast to SA, the other two derivatives in the crystalline phase are thermochromic while in the disordered phase they are photochromic. The other group of Schiff bases were the compounds with two hydroxyl or methoxyl groups attached to the central phenyl ring, known as the hydroquinone family, bis(phenyliminomethyl)hydroquinone (BPH), its monomethoxy-derivative, 4-methoxy-2,5-bis(phenyliminomethyl)phenol (BPHMe) and dimethoxy-derivative, 1,4-dimethoxy-2,5-bis(phenyliminomethyl) benzene (BPHMe$_2$).

The basic tautomers taking part in the photochromic cycle of the compounds are presented in Fig. 2 for the SAA molecule.



Syn-enol *Anti*-enol



Cis-keto *Trans*-keto

Fig. 2. Structures of the tautomers studied illustrated on the example of SAA.

The *syn-anti* isomerisation occurs in the enol form (with a group –O-H) with respect to the C=N bond, while the *trans-cis* – in the keto form (with a group –C=O) with respect to the C=C bond. Despite the presence of two intramolecular hydrogen bonds, in the deactivation process only the keto form with one proton transferred plays an important role (similarly for BSP and BPH) [H1, H2, H11, P10, P15, P32]. The target photochromic form is the *trans*-keto tautomer.

Fig. 3 presents a typical scheme of decay pathways of the excited Schiff bases studied with the energy relations between different tautomers and their states intermediating in the deactivation. The right hand side presents the photochromic cycle leading to formation of *cis*-keto tautomer (processes (1) and (2)) and its decay to the original form (processes (4) and (5)), while the left hand side presents the competitive decay cycle within the primary form (processes (6) and (7)).

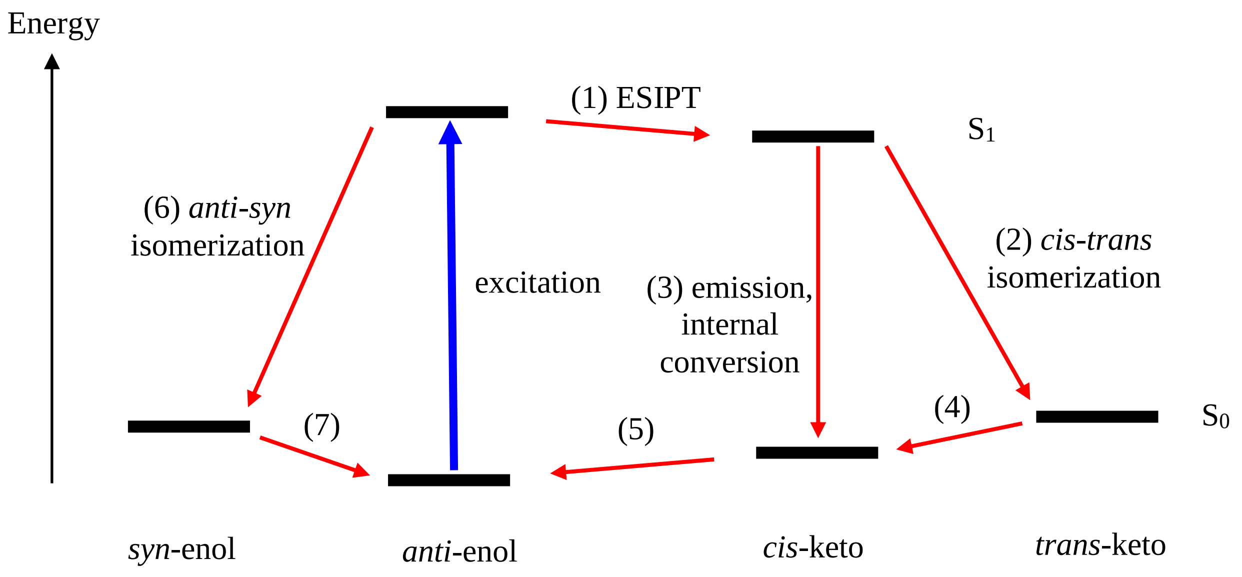


Fig. 3. A typical scheme of decay paths of the Schiff bases studied after photoexcitation. ESIPT is the intramolecular proton transfer in the excited state.

In the following part of this presentation I will describe my most important achievements in the area of Schiff bases studies by the time-resolved optical spectroscopy methods, important from the point of view of the yield and dynamics of the photochromic cycle, reported in the papers [H1-H6, H11].

i) Tautomers in the ground state

For the compounds of interest in a weakly interacting medium the ground state of the lowest energy is the enol form - to be exact the *anti*-enol tautomer, Fig. 3. It is beneficial from the point of view of the photochromic cycle yield (which is the number of molecules transferred from *anti*-enol to *trans*-keto structure related to the total number of excited molecules) as coexistence of many forms in the ground state decreases the selectivity of switching between two states. In the solvents of strong proton-donor properties, such as alcohols, in particular trifluoroethanol (TFE) and hexafluorisopropanol (HFIP), I observed that the *cis*-keto form (with absorption band shifted towards longer wavelength with respect to that of the enol form) is stronger stabilised, which leads to the enol-keto equilibrium in the ground state. The same holds true for all Schiff bases I studied ([H1,H4,H5] and [P15]) except for SAA [H2]. For example, the strongest stabilisation was noted for BSP in HFIP, in which the ratio of keto to enol absorbance was 0.72 [H4]. The character of stabilisation was confirmed by the semi-empirical calculations [H4] and DFT calculations [H5,H11] for the molecules of Schiff bases connected with alcohol molecules via a hydrogen bond. The study of BSP absorbance as a function of HFIP concentration in methanol (MeOH) has shown that the formation of such a complex may involve more than one molecule of HFIP [H4]. The temperature study reported in [H5] have shown that for BSP and BPHMe the difference in enthalpy between the S_0 states of keto and enol forms changes from a positive to negative value at the replacement of MeOH by TFE and the corresponding increase in the proton donating ability of the solvent, e.g. parameter α in the Kamlet-Taft scale.

The shift of the equilibrium in the ground state towards other forms than enol was also observed in heterogeneous media such as micelles [H2, H3], zeolites ([H3] and [P25]) and mesoporous molecular sieves of MCM-41 type [H3]. In these systems the *cis*-zwitterionic or cationic species appeared. It should be mentioned at this point that irradiation of such forms in solid state, reported in [H3] led to changes in colour but the changes were optically irreversible. A very important finding reported in [H1-H3] was Schiff basis decomposition as a result of hydrolysis. It happens in the above mentioned media in which enol tautomer is not the only species in the ground state and in the presence of even trace amounts of water. From among the systems I studied the most resistant to hydrolysis was SAA [H2].

ii) Dynamics of proton transfer in excited state

The excited state intramolecular proton transfer, ESIPT, initiates the photochromic process and is accompanied by a changes in the molecule conformation from *anti*-enol to *cis*-keto species (process (1) in Fig. 3). From the point of view of the yield of photochrome formation, the rate of this process should be high enough to compete with the other channels of S_1 state of *anti*-enol tautomer decay. In the earlier works [P9, P10, P15, P16] we found out that the time of proton transfer in solution is shorter than 50 fs for SA, SAA, BSP and BPHMe (in the latter a small contribution can be brought by the slower path of proton transfer). In [H1] on the basis of the dynamics of growth of transient absorption signals of *cis*-keto BPHMe (<100 fs), I proved that this time does not depend on the polarity and proticity of the solvent. I also proved a tenfold smaller yield of *cis*-keto species formation of BPH which differs from BPHMe by the two intramolecular hydrogen bonds (Scheme 1). It means that for the hydroquinone family of Schiff bases the symmetry of the system significantly decreases the yield of the photochromic cycle.

In [H6] I confirmed the ultrafast (<80 fs) proton transfer in SAA on the basis of direct measurements of fluorescence decay of the primary enol form. I also checked that this ultrafast time does not change in protic solvents or solvents of higher viscosity. In [H4] I applied a strongly proton-donating solvent (HFIP) for BSP and noted the appearance of an additional channel of proton transfer (besides the process of <50 fs) characterised by the time constant 400 fs. The occurrence of this process was manifested as an additional slower growth of absorption signals from S_1 state of *cis*-keto tautomer knowing that such a growth cannot originated from the vibrational relaxation in S_1 state. The most probable explanation of the appearance of such a slower channel is the proton transfer via the solvent molecule, i.e. instead of purely intramolecular process, a hydrogen atom from BSP is transferred to HFIP, while a different hydrogen atom from HFIP is transferred to BSP. This process is possible because the intermolecular hydrogen bond leads to formation of a strong complex of HFIP and BSP.

iii) Dynamics of photochromic species formation

The rate of photochrome formation depends on the decay time of its precursor, so the excited state of *cis*-keto species (processes (2) and (3) in Fig. 3). As follows from theoretical calculations (also in [P32] in which I participated), this state decays by *cis*-trans isomerisation involving a rotation about the C=C bond of the keto species and a consequent closeness of the energy of S_1 state of *cis*-keto species in the rotated geometry to that of S_0 state of *trans*-keto species, e.g. in the form of conical cross-section [4]). A rotation of this type demands breaking up of the intramolecular hydrogen bond and needs overcoming of a certain energy barrier. The decay time of excited *cis*-keto species I studied mainly by the time-resolved emission measured on the fluorescence band corresponding to *cis*-keto tautomer.

In [H2] I performed a comprehensive analysis of time constants of fluorescence decay of SAA in over 10 homogeneous solvents, getting the values from 19 to 140 ps. According to my observations, this time is the shortest in polar and non-protic solvents, e.g. 19 ps in acetonitrile (ACN) and increases with decreasing polarity, e.g. 76 ps in n-hexane (HEX) or with increasing proton-donating properties of the solvent, e.g. 47 ps in TFE. This time also increases with increasing polarizability of the medium depending on the light refraction index of the medium. This means that the energy barrier of the rotation about the C=C bond increases with increasing proticity or polarizability of the medium. Increasing viscosity η of the homogeneous medium leads to increasing time of overcoming the barrier but the lifetime τ dependence on η is weaker than expected from the the linear relation $\tau \propto \eta$. In micellar systems the lifetime of *cis*-keto species increases to about 240 ps for cationic micelles CTAB because of the restrictions of the SAA molecule motion inside a micelle.

For the hydroquinone family of Schiff bases, the lifetime τ dependence of the parameters of the medium is a bit different. In [H1] I reported the shortest lifetimes for nonpolar solvents (280 ps for BPHMe/HEX), while longer in polar ones (480 ps for BPHMe/ACN). Besides, for BPHMe it was significantly longer (by one order of magnitude on average) than for SAA and BSP from the family of salicylideneaniline.

A direct comparison of behaviour of compounds from these two families was the subject of my studies in [H5], where I reported the temperature dependencies of fluorescence kinetics for BSP and BPHMe (as well as for BPH although as mentioned above, the yield of *cis*-keto species formation is very small for this compound). It was proved that the rate constant of non-radiative decay of *cis*-keto species is composed of two terms. One of them is temperature independent (most probably related to internal conversion of S_1-S_0) while the other one shows a temperature dependence of the type $k=A\,e^{-\Delta E/RT}$, and is related to the overcoming of the potential barrier ΔE accompanying structural changes (rotation about the C=C bond). The latter process is by far dominant at room temperature. Interestingly, the difference in the decay rate between BSP and BPHMe is not related to the height of the potential barrier ΔE (which is similar for both compounds and equal to about 4.5 kcal in chloropropane), but the pre-exponential factor A. Most probably the potential barrier as a function of the coordinate of *cis*-trans isomerisation reaction is narrower for a rotation of the terminal phenyl ring (in BSP) than the central phenyl ring (in BPHMe). On measuring the quantum yield and fluorescence lifetime I did not observe changes in the radiative constant as a function of temperature for BSP, BPHMe and BPH. Taking into regard that the yield of *cis*-keto species formation is smaller than 1 (about 0.5 for BSP and BPHMe, 0.05 for BPH), it suggests the barierless nature of *cis*-keto species formation from the primary enol form by ESIPT and of a competitive decay in the enol species (which will be discussed below). It is consistent with the ultrafast dynamics of these processes and shows that temperature cannot change the yield of *cis*-keto species formation for these compounds.

I should mention at this place that the kinetics of fluorescence decay, which I determined many times, were much better approximated by a biexponential than mono-exponential function. It was particularly well pronounced for long decays, e.g. in micelles [H2] or in low temperatures [H2] and for hydroquinone family [H1]. This observation may indicate the involvement of more than one *cis*-keto conformer in the system's deactivation. Unfortunately, very similar spectral dependencies of both components of decay does not permit drawing more detail conclusions. For the fluorescence of anionic form of Schiff bases the situation was different. As reported in [H6] for SAA the amplitudes of individual components of emission decay (two or even three in a viscous solvent) were well separated spectrally, from the fastest in the short-wavelength part of the spectrum to the slowest of the main contribution in the long-wavelength part of the emission spectrum. This fact permitted to conclude that there is a high probability that SAA anion decays via a few successive conformers of increasingly stabilised energetic structure in the excited state.

On the basis of the femtosecond transient absorption measurements we determined the quantum yield of photochromic state formation. For all Schiff bases studied (except for BPH) it reached 10-20% [H1, P10, P15].

iv) Photochromic species lifetime

One of my most important achievements reported in the series of works H was determination of the mechanism of decay of the photochromic (*trans*-keto) tautomers of the Schiff bases studied and the dynamics of return to the original form. This mechanism proved to be rather complex. In [H3] I studied it for BSP (the problem was developed later in [P32]), while in [H2] and [H11] for SAA. Less detail results but confirming the general tendency were also obtained for BPHMe in [H1].

In the solvents not forming hydrogen bonds the photochromic tautomer decays via co-occurring first and second order reactions. The first order reaction characterised by the rate constant k_1 is most probably related to the intramolecular back *trans-cis* isomerisation about the C=C bond in the ground state (process (4) in Fig. 3) while the second order reaction characterised by the rate constant k_2 depends on the concentration of the photochrome, so on the initial concentration of Schiff bases in solution and on the intensity of the pumping pulse. For the typical concentrations used in solutions the second order reaction dominates. The mechanism of this reaction most probably involves the formation of a complex of two *trans*-keto tautomer molecules, double intramolecular proton transfer and formation of twisted enol species. These enol species quickly return to the original forms because the double bond C=C in the keto species becomes a singular C-C bond in the enol tautomer (this process is not shown in Fig. 3). The rate constants of the two reactions decrease with increasing polarity of the medium because of increasing energetic stability of the photochromic tautomer. For example for SAA in HEX the rate constants are: $k_1=1\times10^4$ s^{-1} and $k_2=1\times10^{10}$ M^{-1} s^{-1} (close to the rate of diffusion controlled processes), while in ACN: $k_1=1.5\times10^3$ s^{-1} and $k_2=0.7\times10^9$ M^{-1} s^{-1}. Increasing viscosity hinders the second order process because of restricted rate of diffusion but the rate constant k_1 shows only small changes with viscosity. That is why the photochrome lifetime was not drastically increased on SAA incorporation in polyethylene polymer as k_1 decreased only by one order of magnitude with respect to its value in HEX.

The dynamics of the photochrome deactivation in protic media is equally interesting. In such media the photochrome decay is significantly faster, the reaction of decay becomes a pseudo-first order and the photochrome lifetime is the shorter the stronger are the proton donating properties of the solvent. The mechanism of this decay most probably involves a similar intermolecular proton exchange as in the second order reaction discussed above leading to reduction of the multiplicity of C=C bond. On the basis of measurements for BSP in alcohols of different concentrations, the photochrome decay occurs via formation of a complex of one molecule of Schiff base and one molecule of alcohol. As shown on the basis of measurements for SAA, the same mechanism but with water molecules is responsible for the fast decay of photochrome in normal micelles. Instead of the expected decrease in the rate of photochrome decay following from the restriction of Schiff base motion inside the micelles, it was as high as $k_1=2\times10^6$ s^{-1} (or higher).

v) Decay in enol forms competitive to the photochromic cycle

From the point of view of Schiff bases application in optical memories or switches, my studies of the decay of the primary enol species by a pathway competitive to proton transfer in excited state were especially interesting. This competitive process was proved to significantly reduce the yield of the main photochromic cycle and to lead to the formation of a long-lived tautomer absorbing in the UV range - in contrast to the photochromic tautomer absorbing in the visible range.

The existence of such a channel for all Schiff bases studied I deduced on the basis of the presence of transient absorption signals when there is no longer photochrome in flash photolysis measurements [H1, H4, H11], similar long-lived bands for the reference derivatives of dimethoxy $BSPMe_2$ and $BPHMe_2$ (in which proton transfer cannot take place but in which there is a channel of deactivation in the enol forms [H1, H4]), and ultrafast decays observed for dimethoxy derivatives ([H1] and [P15]). These observations imply that the deactivation of S_1 state of the enol species takes place in a comparably short time as proton transfer (100 fs or shorter). Initially I assigned this ultrashort process to a transition from (π,π*) state to (n,π*) state [H1, H4], but the results of our recent calculations and experiments [P32] indicate that probably the rotation about the C=N bond and the following *anti*-*syn* isomerisation (process (6) in Fig. 3) can take place practically with no barrier (similarly as in SA [4]).

Equally important is the fact that *syn*-enol tautomer in the ground state formed as a result of the above deactivation has a lifetime for s few seconds to a few hours (process (7) in Fig. 3) [H11], so it lives longer than the photochrome tautomer (*trans*-keto). Therefore the decay within enol species not only decreases the yield of the photochromic cycle but also leads to formation of a long-lived transient state competitive to the photochrome. For BSP and BPHMe I estimated relative quantum yield of formation of *syn*-enol and *trans*-keto tautomers in a single cycle as about 1:1 [H1, H4]. For BPH, the amount of *syn*-enol tautomer is about 10 times greater than that of *trans*-keto [H4]. For SAA the quantum yield of *syn*-enol ground state formation is 10 times smaller than that of photochrome formation [H2], but its surprisingly long lifetime being a consequence of stabilisation by an additional intramolecular hydrogen bond, see Fig. 2, leads to accumulation of a significant population of this state in the conditions of stationary irradiation, e.g. 30% in a nonpolar medium under irradiation with a few mW per cm^2 [H11].

C) Triphenylamines and solar cells

In the area of studies of dye-sensitized solar cells (DSSC) with the use of triphenylamines, I concentrated on TPC1, TPC3 and TPC5 dyes whose structural formulae are presented in Fig. 4. The dyes were obtained within the cooperation with research groups of Prof. Licheng Sun from the Royal Institute of Technology in Stockholm and Dr. Xichuan Yang from the Dalian University of Technology. These dyes have a characteristic structure made of three modules: the electron donating part which is a triphenylamine unit, the oligophenylenevinylene bridge whose structure is different in different compounds and the cyanoacrylic acid group which is an electron acceptor and an element attaching (via -COOH) to the surface of semiconducting metal oxides.

DSSC belong to a new and promising generation of solar cells whose potentially smaller cost and higher efficiency in the conditions of medium and low intensity illumination make them an important alternative to the hitherto used silicon solar cells [5,6]. The mechanism of their activity is based on the interaction of the dyes with semiconducting nanostructures, usually titanium dioxide (TiO_2), making a mesoporous layer of very large active surface area. The photoexcitation of the dye leads to injection of an electron to the conduction band of the nanomaterial through which this electron is directed to one of the electrodes, while the missing charge in the dye is compensated for by an electron from the opposite electrode via the electrolyte.

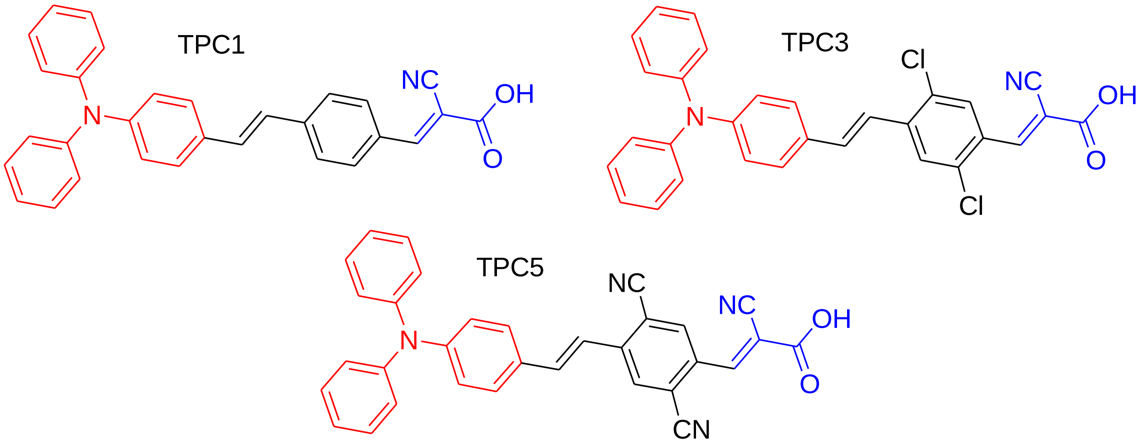


Fig. 4. Structures of triphenylamine compounds studied (the red colour indicates triphenylamine group, the black one - oligophenylenevinylene group and the blue one – cyanoacrylic acid group).

The compounds studied were applied in prototypic solar cells whose sunlight conversion efficiency in standard conditions were 5.3 % for TPC1, 3.9 % for TPC3 and 0.4 % for TPC5 [7]. The aim of my study was to check the dynamics of charge transfer within the molecules of TPC1, TPC3 and TPC5, the rate of electron injection to different nanostructures of titanium dioxide and the undesirable recombination of the electrons from the semiconductor to the dye. The charge transfer processes are schematically shown in Fig. 5. My study was aimed at relating the parameters obtained in laser spectroscopy measurements with the resultant efficiency of the solar cells.

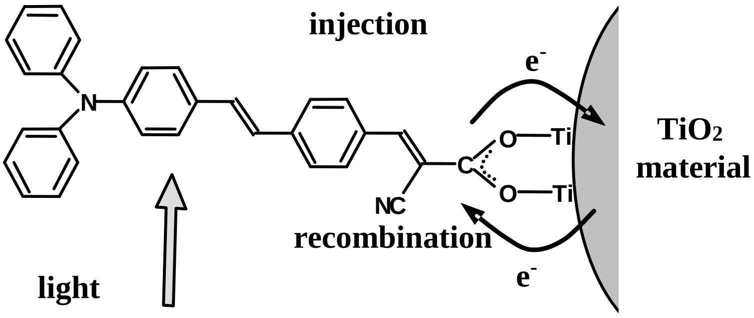


Fig. 5. A scheme of photoinduced electron injection and its recombination in the TPC1 interaction with titanium dioxide.

i) Dynamics in solution

The study reported in [H7] investigate TPC1 and its anionic form in a few homogeneous solvents. I determined the lifetime of excited state of the dyes to vary from 80 ps in ACN to 1.8 ns in HEX. A very high change in the dipole moment at the transition from the ground to excited state (by about 40 D) means that the excited state with charge transfer (CT) is strongly energetically stabilised in a polar medium. As will be shown below, the final position of this state is important from the viewpoint of electron injection efficiency. By ultrashort emission measurements I proved that the locally excited state (LE) decays within 200 fs to CT state whose energy decreases in the solvation process at the time constant from 25 ps in ethanol to below 1 ps in ACN. The molecules of TPC1 was observed to easily convert into anionic form in the solvents of proton-accepting properties (parameter β in the Kamlet-Taft scale; the higher β, the more of the anionic form) because of a strong acidity of the hydrogen from the carboxylic group (-COOH). I proved that with increasing relative population of the anionic form to that of the neutral form in the solution used for sensitization of the nanomaterial, the resultant efficiency of the solar cell decreases.

ii) Interactions with nanostructures in a suspension

In [H8] I included the interaction of TPC1 with nanostructures of titanium dioxide in the form of a suspension in solution. In [H8] I reported the interactions with nanoparticles, nanorods and nanotubes of titanium dioxide studied by the femto- and picosecond emission and absorption spectroscopy. The nanomaterials were obtained from the group of Prof. Maria

Teresa Martínez from the Instituto de Carboquímica, CSIC in Zaragoza. I observed a very efficient shortening of S_1 state lifetime of the dye (compared to the dye's lifetime in the neat solvent) taking place upon electron injection to the semiconductor. Such electron transfer took place according to a multi-exponential function with the main component of 100 fs corresponding to electron injection from high excited vibration levels of S_1 state of the dye. The injection from the relaxed levels took place with the time constants 1-10 ps for nanoparticles and nanorods and 1-3 ps for nanotubes. The short time constant in nanotubes can follows from the effect of confinement of TPC1 molecules in nanotubes of the inner diameter of about 8 nm. I also proved that for the laser pulse energies used (20 mJ/cm^2, which leads to the presence of many injected electrons per nanoparticle) in times of picoseconds an effective recombination takes place leading to a reduction in the population of the injected electrons in the semiconductor to about 20-30% at 1 ns after the excitation.

The subject of [H9] was the interaction of TPC1 with titanium dioxide admixtured with mesoporous silicates of the MCM-41 type (TiO_2-doped mesoporous molecular sieves) provided by Prof. Hermenegildo García from the Instituto de Tecnología Química CSIC-PV in Valencia. In such systems I also observed very efficient quenching of emission from S_1 state of the dye. I compared the results obtained for the two methods of admixturing: grafting leading to formation of titanium dioxide domains in the walls of MCM-41 and impregnation leading to incorporation of titanium dioxide nanoparticles into the structure of the mesoporous material. The method of grafting proved much more effective as it ensured that the rate of electron injection was comparably short as in pure titanium dioxide, while in the method of impregnation the injection was from 2 to 3 times slower. Moreover, when the impregnation method was applied, the maximum content of TPC1 per Ti atoms was almost ten times smaller. I also noted that the lifetime of TPC1 in the materials studied shortened not only because of the electron injection to TiO2 but also as a result of intermolecular energy transfer I also observed in pure MCM-41.

iii) Interaction with nanostructures in thin films in solid state

The final achievement reported in this series of papers was investigation of the interaction of triphenylamines with films of nanoparticles and vertically oriented nanotubes deposited on conducting glass plates [H10] provided by Prof. Craig Grime from the Flux Photon Corporation, USA. Such a system is used as one of the electrodes in DSSC. The nanotubes diameter was 36 or 70 nm, while the thickness of the film was 0.8 or 2 μm. In [H10] I extended the range of studies over the other two compounds (TPC3 and TPC5) and the reference nanoparticles of aluminium oxide (in them electron injection cannot take place because the conduction band has much higher energy than that of titanium dioxide) and I enlarged the time range of the signals studied to milliseconds thanks to the measurements by flash photolysis method.

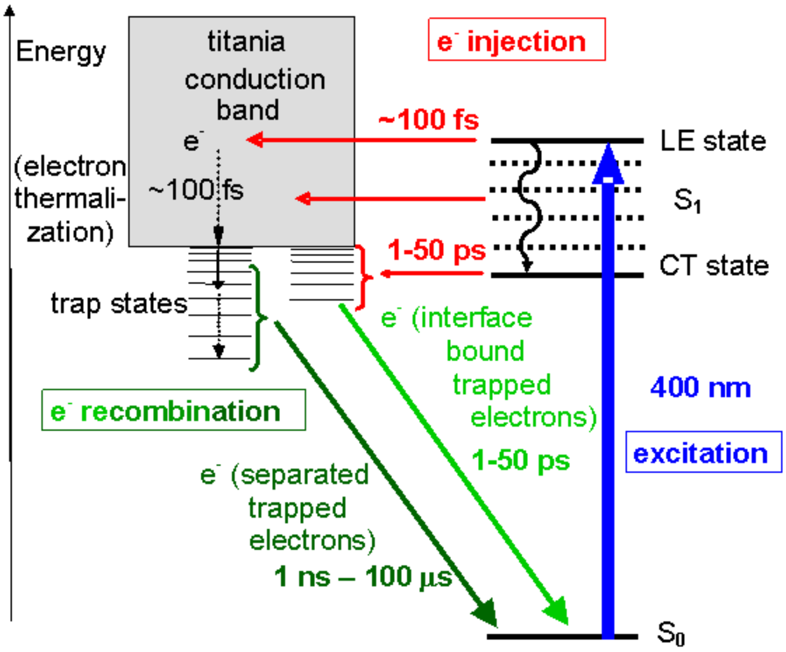


Fig. 6. A scheme of photoinduced charge transfer processes in the system TPC1-TiO_2 nanoparticles [H10].

A scheme of the processes observed and their dynamics for TPC1 (giving the highest solar cell efficiency) is presented in Fig. 6. The types of dynamics obtained in the time range studied were very close for nanoparticles and nanotubes.

Because of a high density of states in the conduction band, the electron injection from LE states and hot CT states is very fast for TPC1, in about 100 fs. However, the competitive processes of vibrational relaxation and solvation brings some part of the population to the relaxed CT state which is near or below the edge of the conduction band of TiO_2. The injection from this level is much slower (on average in 3 ps) and leads to the trap states localized close to the dye. From such trap states a fast recombination takes place (TiO_2 → dye) in the time of 1-50 ps manifested as bleach recovery in transient absorption measurements. It is an undesirable process that can significantly decrease the solar cell sunlight conversion efficiency. The electrons injected directly to the conduction band relax to the trap states localized farther from the dye from which the injection took place. Their recombination is much slower and takes place in the time from 1 ns to 100 μs, with the kinetics described by a stretched exponential function.

In [H10] I have also shown that in TPC3 and TPC5 the time of electron injection is 2-3 times increased, both from LE and CT state. In combination with a fast recombination it leads to a decrease in the quantum yield of electron injection from 80-90% for TPC1 to 50-60% for TPC3 and TPC5. The latter dyes differ from TPC1 by the presence of substituents in the bridge joining the triphenylamine unit with the cyanoacrylic acid group (Fig. 4), which can hinder the charge transfer within the molecule. The substitution was intended to get the absorption band shifted towards longer wavelengths to achieve a better coincidence of the dye absorption band with the solar spectrum and hence a higher efficiency of the solar cell [7]. However, the absorption coefficient of TCP3 and TPC5 lower than that of TPC1 and the lower efficiency of electron injection shown by me have proved that this method of optimisation of solar cells performance is ineffective.

D) Summary

The most important conclusions following from the results published in the series of papers [H1-H11] are:

i) In the photochromic systems studied there is an effective channel of ultrafast deactivation leading to a decrease in the yield of photochrome formation and to the formation of a long-lived individuum absorbing in ultraviolet (*syn*-enol, Fig. 3).

ii) The lifetime of photochromic species is significantly shortened as a result of formation of dimers and complexes with the environment molecules interacting through intermolecular hydrogen bond. Attempts have been undertaken to stabilise the photochromic form in many structures imposing restrictions on free rotation of the molecules (micelles, zeolites, mesoporous materials, polymer). Because of hydrolysis, a number of forms in the ground state, insufficient influence of the environment viscosity and for the reasons mentioned above (intermolecular interaction), the attempts at obtaining a system with the photochromic form lifetime of a minute or longer have failed.

iii) The influence of different parameters of the medium on the dynamics of particular stages of the photochromic cycle and its total yield was specified.

iv) In triphenylaamine dyes used in DSSC, a fast (the fastest component of an order of 100 fs) electron injection to the conduction band of titania nanostrustures was observed.

v) Significant stabilisation of the relaxed charge-transfer state in the dye-titania systems slowing down the electron injection was noted. If the energy of this charge-transfer state is below the edge of titania conduction band, a fast recombination reducing the efficiency of the solar cell can take place.

vi) It was observed that modification of structures of the dyes studied aimed at extension of their long-wavelength absorption leads to slowing down of the electron injection and to a decrease in the quantum yield of this process. It is one of the reasons why such a strategy of modification would lead to reduced efficiency of the solar cell.

It should be emphasised that the work I present as the basis for the habilitation degree procedure was carried out with the employment of many measuring methods used in contemporary photophysical and photochemical research on modern molecular systems. Interestingly, my adventure with the photochromic Schiff bases started about 10 years ago from the measurements of times of the fastest femtosecond processes in which I used my experience in the physics of lasers generating ultrashort pulses. In my further work I developed my experimental skills by other methods bordering on physics and chemistry and related to optical spectroscopy in increasingly longer time scales. My last paper on the Schiff bases [H11] concerns analysis of the processes taking place in the scale of minutes, and from the perspective of a comprehensive approach to the application of such systems I consider it no less valuable as the papers reporting the femtosecond scale study.

The methods I used included the steady state fluorescence (also for determination of fluorescence quantum yields) and absorption in UV-VIS range and partly in the infrared range, also the solvatochromic measurements. The time-resolved absorption measurements I performed in the femto- and picosecond range (transient absorption), nano-, mikro- and millisecond ranges (known as the flash photolysis system) and by a stationary absorption spectrometer for the times from a few seconds to a few hours, all in the UV-VIS range. The time-resolved emission measurements were made by a Time-Correlated Single Photon Counting (TCSPC) system in the pico- and nanosecond range and by the up-conversion method in the femto- and picosecond range. Temperature measurements of the emission and absorption spectra and time- resolved TCSPC measurements were performed in the range 160-320 K. For fitting of the kinetics in time-resolved measurements I used the convolution with instrument response function, also with the instrument response function varying with the wavelength of observation [P5], I applied the global methods of transient absorption analysis and constructed the time-resolved emission spectra (TRES), on the basis of the kinetics of fluorescence decay. The kinetics measured I modelled with the help of mono- and multi-exponential functions, stretched exponent and functions describing mixed decay of the first and second order. I also performed quantum-mechanical calculations using the semi-empirical and DFT methods.

Six compounds of potential use in optical memories I studied in over ten homogeneous solvents of different polarity, viscosity, proton-donating and proton-accepting properties and in a few mixtures, three micellar systems, a few microporous and a few mesoporous molecular sieves (zeolites and MCM-41), and also, to some extend, in solid state and polymer. Three compounds of potential application in solar cells I studied in a few homogenous solvents and in suspensions in which they interacted with different inorganic nanostructures (nanoparticles, nanotubes and nanorods made of titanium oxide) and four different nanostructures in the form of thin films deposited on glass plates (titanium and aluminium oxide nanoparticles, nanotubes of titanium oxide of different diameters). Half of the papers submitted as the basis of habilitation degree procedure (5 fully and 1 in the major part) report results obtained on the measuring equipment from Poznan. Another part was a result of my intense collaboration with the group of Prof. A. Douhal from Toledo.

E) *References*

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All papers co-authored by the applicant:

No.	Paper	IF
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P2	R. Naskręcki, M. Lorenc, M. Ziółek, J. Karolczak. J. Kubicki, M. Szymański, A. Maciejewski, *Transient absorption experimental set-up with femtosecond time resolution*, Bull. Pol. Acad. Sci., Chemistry, **47** (1999) 333.	0.325
P3	A. Maciejewski, R. Naskręcki, M. Lorenc, M. Ziółek, J. Karolczak, J. Kubicki, M. Matysiak, M. Szymański, *Transient absorption experimental set-up with femtosecond time resolution. Femtosecond and picosecond study of DCM molecule in cyclohexane and methanol solution,* J. Mol. Struct., **555** (2000) 1	0.849
P4	K. Gibasiewicz, R. Naskręcki, M. Ziółek, M. Lorenc, J. Karolczak, J. Kubicki, J. Goc, J. Miyake, A. Dobek, *Electron transfer in the reaction center of the photosynthetic bacterium Rb. Sphaeroides R-26 measured by transient absorption in the blue spectral range*, J. Fluoresc., **11** (2001) 33	0.702
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P7	M. Ziółek, R. Naskręcki, M. Lorenc, J. Karolczak, J. Kubicki, A. Maciejewski, *The influence of the excitation geometry on the temporal resolution in femtosecond pump-probe experiment,* Opt. Comm., **197** (2001) 467	1.354
P8	M. Lorenc, M. Ziółek, R. Naskręcki, J. Karolczak, J. Kubicki, A. Maciejewski, *Artifacts in femtosecond transient absorption spectroscopy,* Appl. Phys. B, **74** (2002) 19	2.080
P9	M. Ziółek, J. Kubicki, A Maciejewski, R. Naskręcki, A. Grabowska, *Excited state proton transfer and photochromism of an aromatic Schiff base. Pico- and femtosecond kinetics of the N,N'-bis(salicylidene)-p-phenylenediamine (BSP),* Chem. Phys. Lett., **369** (2003) 80	2.438
P10	M. Ziółek, J. Kubicki, A Maciejewski, R. Naskręcki, A. Grabowska, *An ultrafast excited state intramolecular proton transfer (ESPIT) and photochromism of salicylideneaniline (SA) and its “double” analogue salicylaldehyde azine (SAA). A controversial case,*	2.076

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P13	E. K. L. Yeow, M. Ziółek, J. Karolczak, S. V. Shevyakov, A. E. Asato, A. Maciejewski, R. P. Steer, *Sequential Forward S2-S2 and Back S1-S1 (Cyclic) Energy Transfer in a Novel Azulene-Zinc Porphyrin Dyad,* J. Phys. Chem. A, **108** (2004) 10988	2.639
P14	M. Ziółek, N. Pawlowicz, R. Naskrecki, A. Dobek, *Electron Transfer in the Reaction Center of the Rb. sphaeroides R-26 Studied by Transient Absorption,* J. Phys. Chem. B, **109** (2005) 18171	4.033
P15	M. Ziółek, J. Kubicki, A Maciejewski, R. Naskręcki, A. Grabowska, *Enol-keto tautomerism of aromatic photochromic Schiff base N,N'-bis(salicylidene)-p-phenylenediamine: Ground state equilibrium and excited state deactivation studied by solvatochromic measurements on ultrafast time scale,* J. Chem. Phys., **124** (2006) 124518	3.166
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P17	A. Łukaszewicz, J. Karolczak, D. Kowalska, A. Maciejewski, M. Ziółek, R. P. Steer, *Photophysical processes in electronic states of zinc tetraphenyl porphyrin accessed on one- and two-photon excitation in the soret region,* Chem. Phys., **331** (2007) 359	1.805
P18	M. Ziółek, G. Burdziński, K. Filipczak, J. Karolczak, and A. Maciejewski, *Spectroscopic and photophysical studies of the hydroquinone family of photochromic Schiff bases analyzed over a 17-orders-of-magnitude time scale,* Phys. Chem. Chem. Phys., **10** (2008) 1304	4.064
P19	M. Ziółek, K. Filipczak, A. Maciejewski, *Spectroscopic and photophysical properties of salicylaldehyde azine (SAA) as a photochromic Schiff base suitable for heterogeneous studies,* Chem. Phys. Lett. **464** (2008) 181	2.169

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P21	M. Ziółek, G. Burdziński, J. Karolczak, *Influence of Intermolecular Hydrogen Bonding on the Photochromic Cycle of the Aromatic Schiff Base N,N'-Bis(salicylidene)-p-phenylenediamine in Solution,* J. Phys. Chem. A, **113** (2009) 2854	2.899
P22	K. Gibasiewicz, M. Pajzderska, M. Ziółek, J. Karolczak, A. Dobek, *Internal electrostatic control of the primary charge separation and recombination in reaction centers from rhodobacter sphaeroides revealed by femtosecond transient absorption*, J. Phys. Chem. B **113** (2009) 11023	3.471
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P24	M. Ziółek, M. Gil, J. A. Organero, A. Douhal, *What is the difference between the dynamics of anion- and keto-type of photochromic salicylaldehyde azine?* Phys. Chem. Chem. Phys. **12** (2010) 2107.	3.454
P25	M. Gil, M. Ziółek, J. A. Organero, A. Douhal, *Confined Fast and Ultrafast Dynamics of a Photochromic Proton-Transfer Dye within a Zeolite Nanocage* J. Phys. Chem. C **14** (2010) 9554.	4.524
P26	M. Ziółek , X. Yang, L. Sun, A. Douhal, *Interrogating the ultrafast dynamics of an efficient dye for sunlight conversion* Phys. Chem. Chem. Phys., **12** (2010) 8098.	3.454
P27	A. Synak, M. Ziółek, J. A. Organero, A. Douhal, *Femtosecond Dynamics of a Porphyrin Derivative Confined by the Human Serum Albumin Protein,* J. Phys. Chem. B **114** (2010) 16567.	3.603
P28	M. Ziółek, I. Tacchini, M. T. Martínez, X. Yang, L. Sun, A. Douhal, *Photo-induced electron transfer study of an organic dye anchored on the surfaces of TiO2 nanotubes and nanoparticles*, Phys. Chem. Chem. Phys., **13** (2011) 4032.	3.573
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P34	G. De Miguel, M. Ziółek, M. Zitnan, J. A. Organero, S. S. Pandey, S. Hayase, A. Douhal, *Photophysics of H- and J-aggregates of indole-based squaraines in solid state,* J. Phys. Chem. C **116** (2012) 9379.	4.805*
P35	G. De Miguel, M. Marchena, M. Ziółek, S. S. Pandey, S. Hayase, A. Douhal, *Femto- to Millisecond Photophysical Characterization of Indole-Based Squaraines Adsorbed on TiO2 Nanoparticle Thin Films,* J. Phys. Chem. C **116** (2012) 12137.	4.805*
P36	M. Ziółek, G. Burdziński, A. Douhal, *Long-living Structures of Photochromic Salicylaldehyde Azine: Polarity and Viscosity Effects from Nanoseconds to Hours* Photochem. Photobiol. Sci., **11** (2012) 1389.	2.584*
P37	M. Ziółek, C. Martín, L. Sun, A. Douhal, *Effect of Electrolyte Composition on Electron Injection and Dye Regeneration Dynamics in Complete Organic Dye Sensitized Solar Cells Probed by Time-Resolved Laser Spectroscopy,* J. Phys. Chem. C, accepted, DOI: 10.1021/jp3097988	4.805*

* - Impact Factor from 2011

5. Description of the other research achievements

5.1. Authorship and co-authorship of scientific papers

My research work has been described in the total number of 42 papers, of which **37** have been published in journals from the Journal Citation Reports (JCR) base. Nine of these 37 papers have been published before doctorate, while the 28 after doctorate. A detail list of papers is given in the enclosure entitled "List of papers published”.

The total Impact Factor according to the year of publication is 105.98, while the mean Impact Factor is 2.864. The total number of citations is 420 with self-citations and **310** without them (on the basis of ISI Web of Knowledge). My Hirsch index is **H=12**.

From among the 37 papers published in journals from the JCR base, I am the first author or the corresponding author of 21 and the second authors in 8.

5.2 Presentation of reports and communications at international and national conferences

I am a co-author of **42** conference communications, of which **13** I presented myself; 8 of them after doctorate. I delivered about 20 faculty or group seminars. A detail list of communications presented is given in the enclosure entitled "List of conference communications".

Below I present the list of conference communication which I presented myself.

a) Oral communications

1. J. Kubicki, A. Maciejewski, R. Naskręcki, M. Ziółek, A. Grabowska
„*Przenoszenie protonu w fotochromowej zasadzie Schiffa obserwowane w femtosekundowej skali czasu*”
Ogólnopolskie seminarium „Ultraszybkie procesy w fizyce, chemii i biologii” Warszawa, 3.06.2002

2. M. Ziółek, J. Kubicki, A Maciejewski, R. Naskręcki, A. Grabowska,
“*Excited state proton transfer and competitive processes in aromatic Schiff bases*”,
Polish Photoscience Seminar, Warszawa, 16-17.10.2003

3. M. Ziółek, J. Kubicki, A Maciejewski, R. Naskręcki, A. Grabowska,
“*Excited state intramolecular proton transfer reaction and photochromism of the new family of Schiff bases*”,
International Conference on Transient Chemical Structures in Dense Media, Paryż, Francja, 14-16.03.2005

4. M. Ziółek, G. Burdziński, K. Filipczak, J. Karolczak, A. Maciejewski, R. Naskręcki, S. Starkowski,
„*Badanie przenoszenia protonu i indywiduów przejściowych uczestniczących w cyklu fotochromowym hydrochinonowej rodziny zasad Schiffa*”,
XI Mikrosympozjum „Kinetyczne metody badania mechanizmów reakcji w roztworach”, Poznań, 25.05.2007

5. M. Ziółek
„*Wpływ międzycząsteczkowych wiązań wodorowych na cykl fotochromowy zasad Schiffa*”,
Polish Photoscience Seminar, Warszawa, 11-12.06.2008

6. M. Ziółek, M. Gil, J. A. Organero, A. Douhal,
“*Fs dynamics of salicylaldehyde azine structures in solution and within nax/nay faujasite zeolites*”
XXIV International Conference on Photochemistry, Toledo, Spain, 19-24.07.2009

b) Poster presentations

1. M. Lorenc, M. Ziółek, R. Naskręcki, J. Karolczak, J. Kubicki, A. Maciejewski
„*Femtosecond study of DCM molecule in cyclohexane and methanol solution*"
VIth Dutch-Polish Colloquium „Crossroads of Condensed Matter and Opical Physics”, Poznań, 11-12.02.2000

2. M. Ziółek, M. Lorenc, R. Naskręcki
„*Artefakty w femtosekundowej spektroskopii absorpcji przejściowej*”
Mikrosympozjum laureatów konkursu „Fastkin”, Poznań, 22-23.05.2000

3. M. Ziółek, R. Naskręcki, M. Lorenc, J. Karolczak, J. Kubicki
„*The effect of group velocity dispersion on pump-probe type of experiments with femtosecond time resolution*”
Physique en Herbe 2000,
Lille, France, 19-24.06.2000

4. M. Ziółek, R. Naskręcki, M. Lorenc
„*The influence of excitation geometry and sample thickness on the temporal resolution in femtosecond pump-probe experiments*”
ESF-ULTRA spring school on “Ultrafast technology and advanced microscopy applications to intra-cellular and biomolecular dynamics”,
Cargese, Francja, 25-31.03 2001

5. M. Ziółek, R. Naskręcki, J. Karolczak, J. Kubicki,
“*Temporal and spectral properties of the femtosecond supercontinuum under different generation conditions*”,
Ultra School on “Ultrafast processes in Photochemistry and Photobiology”,
Toruń, 25-30.08.2003

6. M. Ziółek, X. Yang, L. Sun, A. Douhal,
“*Forward and back electron transfer in new dyes interaction with titania nanoparticles for solar cell systems*”,
Hybrid and Organic Photovoltaics Conference HOPV 2010,
Assisi, Italy, 23-27.05.2010

7 M. Ziółek, C. Martín, J. A. Organero, M. Navarro, X. Yang, H. Garcia, A. Douhal
“*Studies of new mesoporous materials interacting with an organic dye for the alternative charge collection network in solar cells*”,
Hybrid and Organic Photovoltaics Conference HOPV 2011,
Valencia, Spain, 15-18.05.2011

5.3 Participation in research projects:

1. KBN project no. 2 P03B 136 19: "Investigation and analysis of artefacts appearing in the transient absorption measurements in femtosecond time scale" 01.07.2000 – 30.06.2001 (principal investigator).

2. KBN project no. 2 P03B 040 22: "Analysis of linear and nonlinear physical processes in the femtosecond two-pulse spectroscopy", 01.02.2002-31.12.2003 (principal researcher - PhD grant)
3. KBN project no. 2 P03B 015 24: "Molecular aspects of photochromism. Photoinduced proton transfer in selected Schiff bases studied by ultrafast optical spectroscopy" 20.05.2003 – 19.11.2005 (researcher)
4. MNiSW project no. N204 124 31/2853: "Spectral, photophysical and photochemical properties of some molecular probes. The role of hydrogen bonds, spectroscopically non-observable states and reversible photochemical reaction on the deactivation processes of excited molecules" , 28.09.2006-27.09.2009 (researcher)
5. MNiSW project no. N204 149 32/3777: " Influence of environment on photochromism. Investigation of intramolecular proton transfer and photoinduced structural changes in some aromatic Schiff bases " 20.03.2007-19.03.2010 (principal investigator)
6. Marie Curie grant within the UE 7th Framework Programme (FP7-PEOPLE-IEF-2008 no. 235286: From Femto to Millisecond and From Ensemble to Single Molecule Photobehavior of Some Nanoconfined Organic Dyes for Solar Cells Improvement (NANOSOL), 01.06.2009-31.05.2011 (principal researcher).
7. Project: Strategic Japanese-Spanish Cooperative Program (PLE 2009–0015): Design, exploration and fabrication of solar cells based on new materials with high conversion efficiency (NANOCONV*)*, 01.11.2009-30.12.2013 (researcher).

5.4 Peer reviewing activity

In total I reviewed 16 papers submitted to the journals:

- Physical Chemistry Chemical Physics (6);
- New Journal of Chemistry (5);
- Chemical Physics Letters (2);
- Spectrochimica Acta Part A (1);
- Journal of Physical Organic Chemistry (1)
- Journal of Photochemistry and Photobiology A (1).

I also took part in reviewing over ten manuscripts in the group of Prof. A. Douhal, Toledo.

Apart from the above, I was a reviewer of one international doctoral thesis of Mr Juan Manuel Ortiz Sánchez from the Universitat Autonoma de Barcelona, entitled "Excited state intramolecular proton transfer reactions coupled with non adiabatic processes: Electronic structure and quantum dynamical approach.”. The public defence of the thesis took place on 26.11.2009 in Barcelona.

5.5 Awards

- Stipend of the Minister of National Education for the academic year 1998/99
- Stipend of the Foundation for Polish Science, for young research workers for the years 2002 and 2003
- Award of the AMU Vice Rector in 2005
- AMU Rector Group Award of 3rd degree in 2006
- AMU Rector Award of 2nd degree in 2007
- Marie Curie Grant within the EU 7th Framework Programme, 2009-2011 r.

6. Scientific carrier

Before doctorate

I began my research work in 1998 when I was a 4th year student of physics at the Faculty of Physics, Adam Mickiewicz University, Poznan, (AMU), in the area of ultrafast laser spectroscopy under supervision of late Professor Marian Szymański, at the Quantum Electronics Division. I was learning the operation and testing the possibilities of a newly purchased system for fluorescence lifetime measurements by the method of Time-Correlated Single Photon Counting, (TCSPC) allowing measurements of emission decays to a resolution of single picosecond. This TCSPC system was purchased for the AMU interfaculty Center for Ultrafast Laser Spectroscopy (CBUSL). This first stage of my work resulted in co-authorship of the program for analysis of such emission decays and co-authorship of my first research paper ([P1] in the list in enclosure 5).

After the sudden death of Prof. M. Szymański, Prof. Franciszek Kaczmarek became my supervisor and I was working under the care of Prof. Ryszard Naskręcki. I was learning the operation of the second ultrafast laser spectrometer purchased by CBUSL, which permitted transient absorption measurements to a femtosecond resolution. My master's thesis, defended in June 1999 was entitled "A system for transient absorption measurements to a femtosecond resolution; preliminary and testing measurements". Results of my works have been published in papers [P2] and [P3] describing the performance of this measuring system. Working towards doctorate, promoted by Prof. Ryszard Naskręcki, I was concerned with the problems related to the methods of transient absorption measurements in the femtosecond range. The most important results at this stage of my research work have been published in a series of three papers on (i) determination of correct instrument response function for the case of different velocities of the pump and probe pulses in the sample [P5], (ii) determination of the influence of the geometry of excitation on the instrument response function [P7] and (iii) determination of physical artefacts accompanying measurements in the femtosecond time scale and finding the methods for their minimisation [P8]. The importance of this work is illustrated by the fact that till today the papers [P5] and [P8] published in Appl. Phys. B have been cited nearly 100 times. Till today I consider as one of my greatest conceptual achievements the derivation of a relatively simple analytical formula for the instrument response function, taking into account the group velocity of laser pulses, sample thickness and sample absorption. My doctoral thesis included also a complex program I wrote in PV-WAVE environment for analysis and processing of transient absorption data, in which the above mentioned instrumental problems were taken into account. The program also performed the convolution of the fitted kinetics with the true instrument response function varying for different probe pulse wavelengths.

While working towards my doctorate I was engaged as a chief manager of one-year KBN project for young research workers (2 P03B 136 19), and then as principal researcher of a two-year promoter grant (2 P03B 040 22) and I was awarded a stipend form the Foundation for Polish Science. Apart from analysis of the physical phenomena accompanying transient absorption measurements, I was engaged in investigation of three biological and photochemical systems studied femtosecond transient absorption. These systems were the photosynthetic bacteria R-26 [P4], xanthione from the family of aromatic thioketones [P6] and BSP compound from the family of salicylideneaniline derivatives [P9]. Investigation of BSP were particularly suitable for presentation of the possibilities of the system for measurements in the femtosecond scale (transient absorption decay measurements in the time of 50 fs) and for testing the procedure of proper transient absorption measurements I proposed in my doctoral thesis. The study of this compound has initiated my many year long adventure with z aromatic Schiff bases.

The public defence of my doctoral thesis on “The analysis of linear and nonlinear physical processes in the femtosecond two-pulse spectroscopy” took place in June 2003 and I was awarded the doctor of science degree in physics.

Research work after doctorate

After the doctorate I was employed as an adjunct in the AMU Center for Ultrafast Laser Spectroscopy and then since 2008 till today I have been employed as an adjunct in the Quantum Electronics Division. In the period since the doctor's degree conferment I published 17 papers - apart from those included in the series of works presented as the basis for the habilitation degree procedure. Shortly after the doctorate I extended the area of my interest concerning the white light continuum generation used as a probe pulse in transient absorption measurements, briefly presented already in the doctoral thesis. Results of this research work are published in [P11]. In cooperation with Dr Gotard Burdziński from the Faculty of Physics, AMU, I wrote a paper on ultrafast spectroscopy of another compound from the family of thioketones [P12]. In my later work I did not continue working in these two fields.

The subject that has been hitherto of my main concern was comprehensive investigation of photochromic compounds from the group of Schiff bases, in which the photochromic cycle is initiated by fast proton transfer in the excited state. At first I worked in cooperation with Prof. Anna Grabowska from the Physical Chemistry Institute of the Polish Academy of Sciences, Warsaw, as she has suggested this subject to our group at the Quantum Electronics Division. Together with Prof. Ryszard Naskręcki I worked on UV-VIS transient absorption measurements in the femto- and picosecond range, while Dr. Jerzy Karolczak and Prof. Jacek Kubicki took part in the measurements of fluorescence decays in the picosecond range. Later also Dr. Gotard Budziński took part in the studies and he worked on laser flash photolysis in the nano- and microsecond range. The chemistry of the problem was supervised by Prof. Andrzej Maciejewski from the Faculty of Chemistry, AMU, who was kind enough to introduce me to problems from the area of photochemistry and photophysics of molecular systems in the liquid phase. All time-resolved measurements till 2009 were performed on the equipment of the Center for Ultrafast Laser Spectroscopy, AMU. The studies were partly financed from the two projects: KBN project 2 P03B 015 24 in which I participated as a researcher, and MNiSW project N204 149 32/3777, in which I took part as a chief manager.

Our first papers concerned the fastest proton transfer processes in the photochromic Schiff bases, accompanying transitions from the excited enol conformer to keto conformer and the observation of the keto species fluorescence decay. In [P10] we studied salicylideneaniline (SA), a model compound of aromatic Schiff bases, for which we observed the proton transfer time below 50 fs, which corrected the earlier results of other authors suggesting a longer duration of this process. From the perspective of time, this paper seems very important for understanding of the mechanism of processes taking place in this class of compounds. The proton transfer duration determined by us has been later verified in a few theoretical and experimental works. In [P15] we report the study of BSP in a few solvents, whose application permitted selective excitation of the enol and keto species being in equilibrium thanks to stabilisation of the keto species in the protic solvents. In [P16] we observed the existence of the faster and slower trajectories of proton transfer for the hydroquinone family of Schiff bases. My further papers concerning the studies in this area ([P18]-[P21], [P23], [P24] and [P36]) were included in the series of papers presented as the basis for the habilitation degree procedure and they have been discussed above. I excluded from this series two papers written within my few years cooperation with Prof. Abderrazzak Douhal from the Universidad de Castilla La Mancha in Toledo, Spain, in which my participation was significant but not exceeding 60%. [P25] was concerned with the time-resolved emission measurements of SAA (the symmetric derivative of SA) anchored in microporous molecular sieves (zeolites), while [P32] was devoted to a comprehensive theoretical and experimental analysis of the photochromic cycle of BSP and was written thanks to the cooperation with the groups of Prof. Miquel Moreno and Prof. Jose Llucha from Barcelona. At present I am working on my last paper reporting on the studies of Schiff bases performed in cooperation with Prof. Aleksander Filarowski from the University of Wrocław; the studies concern the APA compound (provided by Prof. Filarowski) which is a modification of SAA.

I was also engaged in time-resolved spectroscopic measurements (mainly the UV-Vis femtosecond transient absorption) in the other two areas. The first was the electron transfer and recombination at the reaction centres of purple bacteria. Within this area, under supervision of Prof. Andrzej Dobek from the Faculty of Physics, AMU, I wrote the paper [P14] and later I cooperated with Dr. hab. Krzysztof Gibasiewicz, the Faculty of Physics, AMU, and on the basis of these studies the paper was written [P22]. The second area was related to investigation of porphyrins. Within the cooperation with Prof. Ron Steer from the University of Saskatchewan, Canada, we studied the dynamics of energy transfer in an interesting system of azulene and zinc porphyrin, reported in [P13]. Then I was engaged in the studies of the deactivation of zinc porphyrin excited to the Soret band, reported in [P17]. In the group of Prof. A. Douhal from Toledo I took part in the studies of the porphyrin interaction with HSA protein, reported in [P27].

In 2009 I received a grant from the Marie Curie Foundation for realisation of the project "*From Femto to Millisecond and From Ensemble to Single Molecule Photobehavior of Some Nanoconfined Organic Dyes for Solar Cells Improvement* (NANOSOL)" and in 2009-2011 for two years I worked at post-doc position in the group of Prof. A. Douhal, Toledo, within this project. Four of the papers written in this period ([P26], [P28], [P29] and [P33]) I included in the series of papers presented as the basis of the habilitation degree procedure. They concerned the properties of dyes from the family of triphenylamines (abbreviated as

TPC1, TPC3 and TPC5) and dynamics of their interactions with nanostructures of titanium dioxide, and have been discussed above. The other papers reporting the results of NANOSOL project realisation were devoted to the interactions of the triphenylamine dyes with nanoparticles of other metal oxides [P30] and comparison of specific dye sensitized solar cells (DSSC) constructed with the use of triphenylamine dyes and nanoparticles of titania or mesoporous materials of MCM-41 type admixtured with titanium dioxide [P31]. In these papers the main task was determination of the rate of electron injection from the dye to the inorganic nanomaterial, the rate of recombination (electron transfer from the nanomaterial to the dye) and the dye regeneration by the electrolyte. In realisation of the NANOSOL project I modified two femtosecond spectrometers for measurements of transient absorption and fluorescence by the method of up-conversion to allow the transmission studies in thin films, and I wrote a program for chirp correction of probe pulse and smoothing of the kinetics obtained from the transient absorption measurements. After completion of the NANOSOL project I continued cooperation with Prof. Douhal and took part in the time-resolved spectroscopic measurements of another family of dyes used in DSSC, i.e. squaraines in the form of thin films on solid state, reported in [P34], and squaraines interacting with nanoparticles of titania, reported in [P35]. These studies were performed within the Spain-Japan project NANOCONV, on the samples provided by the group of Prof. Shuzi Hayase from the Kyushu Institute of Technology, Japan.

In July 2012 I stayed for one month in Toledo to study the influence of the composition of electrolyte in complete functioning solar cells on the rate and efficiency of electron injection. The efficient dye TH305 from the family of triphenylamines was provided by Prof. Licheng Sun from Stockholm. The studies are reported in [P37]. For the last few months I have been working on dye sensitized solar cells based on the indoline dye D149. It is my intention to devote the nearest few years of work to the problems of investigation and optimisation of solar cells of new generation.

Marcin Ziółek
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