

Attachment no 3B

SUMMARY OF PROFESSIONAL ACCOMPLISHMENTS

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Summary of Professional Accomplishments

1. Name and surname

ANNA SYNAK

2. Diplomas, degrees conferred in specific areas of science or arts, including the name of the institution which conferred the degree, year of degree conferment, title of the PhD dissertation

- Doctor of physical sciences in the field of physics
granted by the resolution of the Council of the Faculty of Mathematics, Physics and Informatics of the University of Gdansk, of 18th January 2007
title of the doctoral dissertation: Migration of the electronic excitation energy in uniaxially oriented polymers
promoter: prof. dr hab. P. Bojarski
- graduate diploma of Postgraduate Studies in Fundamentals of Computer Science, 2007
Faculty of Mathematics, Physics and Informatics
University of Gdansk
- Master's degree in education in the field of physics and mathematics
Faculty of Mathematics, Physics and Informatics of the University of Gdansk, 2001 r.
title of the master's thesis: Selected photophysical properties of acrylodan and badan
promoter: prof. dr hab. Piotr Bojarski

3. Information on employment in research institutes or faculties/departments or school of arts

- research and teaching assistant professor (since 3rd March 2010)
University of Gdansk, Faculty of Mathematics, Physics and Informatics, Institute of Experimental Physics
- research assistant professor (02.06.2008 – 30.11.2009)
University of Castilla La Mancha, Maria Skłodowska-Curie scholarship under the 7th EU Framework
Toledo, Spain

4. Description of the achievements, set out in art. 219 para 1 point 2 of the Act

As the scientific achievements referred to in Article 219, paragraph 1, item. 2 of the Act of July 20, 2018, Law on Higher Education and Science (Journal of Laws of 2021, item 478, as amended), I identify a series of thematically related nine scientific articles (H1-H9, listed below), in which the quantitative analysis of the excitation energy transport and its trapping in selected fluorescent systems, such as porous nanolayers, spherical nanoparticles, polypeptides and thin polymer films, is presented. These publications comprise **a scientific cycle entitled:**

**Analysis of electronic excitation energy transfer, excitation energy trapping
and intermolecular aggregation in selected fluorescent systems**

List of publications constituting the habilitation series:

- H1. **A. Synak**, L. Kułak, S. Rangełowa-Jankowska, B. Grobelna, A. Kubicki, P. Bojarski¹, *Reversible energy transfer between monomers and fluorescent dimers of rhodamine S in polyvinyl alcohol films*, *Chemical Physics* **382** (2011) 47-51
DOI: <https://doi.org/10.1016/j.chemphys.2011.02.008>, IF₂₀₁₁ – 1,896
- H2. P. Bojarski, L. Kułak, K. Walczewska-Szewc, **A. Synak**, M. V. Marzullo, A. Luini, and S. D’Auria, *Long-distance FRET analysis: A Monte Carlo simulation study*, *The Journal of Physical Chemistry B* **115** (2011) 10120-10125
DOI: <https://doi.org/10.1021/jp202152m>, IF₂₀₁₁ – 3,696
- H3. **A. Synak**, P. Bojarski, B. Grobelna, L. Kułak, and A. Lewkowicz, *Determination of local dye concentration in hybrid porous silica thin films*, *The Journal of Physical Chemistry C* **117** (2013) 11385-11392
DOI: <https://doi.org/10.1021/jp401839j>, IF₂₀₁₃ – 4,835
- H4. **A. Synak**, B. Grobelna, L. Kułak, A. Lewkowicz, and P. Bojarski, *Local Dye Concentration and Spectroscopic Properties of Monomer–Aggregate Systems in Hybrid Porous Nanolayers*, *The Journal of Physical Chemistry C* **119** (2015) 14419-14426
DOI: <https://doi.org/10.1021/acs.jpcc.5b03501>, IF₂₀₁₅ – 4,509
- H5. **A. Synak**, P. Bojarski, M. Sadownik, L. Kułak, I. Gryczynski, B. Grobelna, S. Rangełowa-Jankowska, D. Jankowski, A. Kubicki, *Excitation energy transfer in partly ordered polymer films differing in donor and acceptor transition moments orientation*, *Optical Materials* **59** (2016) 34-38
DOI: <https://doi.org/10.1016/j.optmat.2016.03.005>, IF₂₀₁₆ – 2,238
- H6. **A. Synak**, R. Fudala, I. Gryczynski, L. Kułak, S. Shah, I.E. Serdiuk, B. Grobelna, P. Arłukowicz, A. Kubicki, and P. Bojarski, *AMCA to TAMRA long range resonance energy transfer on a flexible peptide*, *Dyes and Pigments* **158** (2018) 60-64
DOI: <https://doi.org/10.1016/j.dyepig.2018.05.019>, IF₂₀₁₈ – 4,018
- H7. **A. Synak**, I. E. Serdiuk, B. Grobelna, R. Fudala, I. Gryczynski, P. Bojarski, *Spectroscopic method for estimation of MMP-9 enzyme concentration and activity*, *Journal of Molecular Liquids* **286** (2019) 110936 (5pp)
DOI: <https://doi.org/10.1016/j.molliq.2019.110936>, IF₂₀₁₉ – 5,065

¹ The corresponding author is marked with the envelope symbol

- H8. **A. Synak**, L. Kułak, P. Bojarski, and A. Schlichtholz, *Förster Energy Transfer in Core–Shell Nanoparticles: Theoretical Model and Monte Carlo Study*, *The Journal of Physical Chemistry C* **125** (2021) 18517-18525
DOI: <https://doi.org/10.1021/acs.jpcc.1c05314>, IF₂₀₂₁ – 4,177
- H9. **A. Synak**, E. Adamska, L. Kułak, B. Grobelna, P. Niedziałkowski, and P. Bojarski, *New core-shell nanostructures for FRET studies: synthesis, characterization, and quantitative analysis*, *International Journal of Molecular Sciences* **23** (2022) 1-13
DOI: <https://doi.org/10.3390/ijms23063182>, IF₂₀₂₂ – 5,600

Applicant's contribution to each of the listed papers is described in the Attachment no 4B. Contribution of the co-authors is given in the co-authors statements, Attachment no 5.

PRESENTATION OF THE SCIENTIFIC CYCLE²

Analysis of electronic excitation energy transfer, excitation energy trapping and intermolecular aggregation in selected fluorescent systems

Introduction

Nonradiative electronic excitation energy transfer (NET) is a physical phenomenon that has numerous crucial applications in optical materials, molecular biophysics, biochemistry and nanomedicine [1-8, **H2**, **H7**]. It plays an important role in, among other things, the phenomenon of photosynthesis, provides fundamental information about polypeptide and protein conformations and intramolecular distances in a range of macromolecules, and can be a reliable indicator of their aggregation or breakdown as a result, for example, of enzymes action [9-11].

NET phenomenon occurs both in systems with random arrangement of fluorophores (disordered systems, e.g. solutions) and in those that exhibit some kind of ordering (e.g. biological membranes, liquid crystals, uniaxially oriented polymers) [12-15, **H5**]. Currently, research on nonradiative excitation energy transfer also concerns new challenges formulated in connection with the development of broadly understood nanotechnology, optoelectronics and the design of broadband light sources on the nano and microscale [16-18].

Nonradiative electronic excitation energy transfer in fluorescent systems can take place between either the molecules of the same type or between the different ones. Particles that release excitation energy are called donors (D) while the recipients are called acceptors (A). A prerequisite for energy

² Further, references marked with letter H and a numbers, for example [H1] refer to works constituting the cycle of publications on which the habilitation application is based on. Other references marked with numbers like for example [1] do not constitute this cycle. In order to keep the natural flow of references in the presentation of scientific cycle the numbers of these works are different than those in summary of accomplishments (attachment 4A)

transfer is partial overlap of the fluorescence spectrum of a donor and the absorption one of acceptor. Nonradiative energy transfer occurs at sufficiently small distances between an excited donor D and unexcited acceptor A, ensuring strong enough coupling of the interacting fluorophores. The discussed phenomenon takes place at distances $R_{DA} \ll \lambda$, typically not exceeding 10 nm, where R_{DA} is the distance between the interacting particles, considered as point dipoles, while λ is the wavelength of the wave emitted by a donor particle [19,20].

The intermolecular NET phenomenon between an excited donor and unexcited acceptor was already attempted in the 1920s to be quantitatively described by J.B. Perrin. However, the author of the first complete and positively verified experimentally theoretical works describing the nonradiative electronic excitation energy transfer, in a single step from the donor to the acceptor, by means of the quantum mechanical calculus of perturbations was Theodor Förster in the 1940s [21]. Over the years, it became apparent that of particular importance in the theory he developed was the finding describing the rate constant of the energy transfer in one step from an excited donor to not unexcited acceptor, under the assumption of a dipole-dipole nature of the coupling between the interacting molecules. The expression describing the rate constant (probability of energy transfer per unit time) in this case predicts its dependence on R_{DA}^{-6} , where R_{DA} is the distance between the interacting energy donor and acceptor.

This relationship received by Förster describes very well the direct energy transfer from a donor to acceptor not only in viscous and stiff solutions but also in a vast majority of dichromophoric systems (labeled with two different appropriately selected fluorescent probes polymers, polypeptides, proteins, DNA and other macromolecules).

It can be stated today that the formula obtained by Förster for the rate constant describing energy transfer, in one step, from an excited donor to unexcited acceptor, in case of negligible material diffusion, has stood the test of time and constitutes the foundations for numerous application studies as well as the theory further developments. These developments are of a very diverse nature and are determined by various needs both fundamental and application needs.

The assumption made in the Förster model of a one-step energy transfer from a donor to acceptor implies that in solutions, for example, investigations are limited to low molar donor concentrations with a sufficiently high molar concentration of the acceptor at the same time. When this strict condition is not met, the Förster's theory ceases to describe the experiments correctly, as the direct transfer of energy from a donor to acceptor starts to compete with the phenomenon of multistage excitation energy migration in a set of donors. The necessity to overcome the pointed out limitation (together with some other ones) triggered the development of more general models, in which the Förster's findings appear to be simply a special case.

These models include, among others, the study of the aforementioned multi-step excitation energy transfer in a set of molecules of the same type (donors) before the excitation is transferred to a set of acceptors, the effect of reverse energy transfer from acceptors to donors, the effects of intermolecular correlations in the energy transport process, directional energy transfer in systems with a specific geometry or ordering of the directions of the transition moments of the interacting fluorophores [22-25]. And although these models represent themselves a methodologically diverse class, it turns out that

the dependence of the energy transfer rate constant on distance remains preserved in all of them, regardless of whether the energy transfer is one or multi-step and whether it takes place occurs from a donor to acceptor or vice versa. This common interesting feature indicates Förster's extremely good intuition and the dominant role of dipole-dipole coupling

Of course, there exists also an important group of models describing energy transfer phenomena, for which a different or modified constant rate appears appropriate. These models are exploited, for example, in systems with significant or dominant material diffusion of fluorophores, in strongly coupled donor-acceptor systems with overlapping molecular orbitals, in the photosynthesis phenomenon or in studies of plasmonically enhanced energy transfer [26-30].

Significant advances have taken place in optical materials and nanotechnology in recent years. Functional core-shell nanostructures or nanolayers on metallic substrates containing fluorophores can, for example, serve as local emission amplifiers, elements of biosensors or broadband light sources at a micro or submicroscale [31-33,34,35]. In such systems, the energy transfer between fluorophores localized on fragments of nanostructures can play an important role in designing a particular material with desired properties. However, as it turns out, the quantitative description of energy transfer in such systems is clearly more difficult than in typical disordered ones. This is related to the specific geometry of such systems, which characteristics must be taken into account during modeling trials: e.g. the spatial distribution of fluorophores transition moments in uniaxially oriented thin polymer films, finite number of fluorophores, e.g. on the surface or in volume of a nanostructure, distribution of the area of nanoparticle surfaces, or, in the case of porous nanolayers, preferential filling with fluorophores of small parts of nanostructures, e.g., surface or pore volume [H2-H5, H9]. The above-mentioned facts often lead to serious difficulties in developing analytical models due to the greater complexity of the examined systems. Although in some cases it is possible to develop and positively verify a model that returns as a final result an analytical expression for emission intensity decay, emission anisotropy decay or other luminescence observables, it is much easier to describe the characteristics of complex systems using the Monte-Carlo simulation method [36, 37].

A considerable advantage of using the Monte Carlo simulation method is that it also allows finding of some important parameters characterizing the energy transfer that unavailable directly through measurements, such as: the average value of the orientation factor, the average number of excitation energy jumps in the system, the average squared displacement of excitation or the average time of energy localization on the excited molecules [37]. The analysis of the above quantities allows to accurately assess the influence of various factors (e.g., molecules orientation, geometry of the system) on the studied processes, often deciding about interpretation of the experimental data.

The papers H1-H9 presenting my experimental studies together with quantitative analysis of the obtained results show, based on several examples, the necessity of using diverse approaches to describe the properties of energy transport phenomena as well as the properties of the investigated systems themselves, while preserving the mentioned common foundation of the discussed research, which is the dipole-dipole mechanism of the electronic excitation energy transfer. The analyses performed indicate a very important role of analytical models as well as the Monte-Carlo simulations in description of fluorescent systems studies, with the Monte-Carlo method showing evident advantage in case of higher complexity systems.

Outline of the development of the nonradiative electronic excitation energy transfer theory

NET theory has been particularly well formulated for three-dimensional disordered systems with infinitely large number of fluorophores in a solution (thermodynamic limit). As it has been already mentioned in the introduction, the NET process from an excited donor to an unexcited acceptor takes place in case of sufficiently strong energy coupling of these species and can, in standard cases, occur at distances much smaller than the donor fluorescence wavelength and, at the same time, not larger than 10 nm. Different electron states of the donor and acceptor molecules (mainly singlet and triplet) may be involved in the process, and it may be the result of a Coulomb or exchange interactions [19,21,38,39]. I will discuss the first situation only. Förster related the probability of energy transfer between two molecules to, among other things, the relative position of the acceptor absorption and donor emission spectra, with partial overlap of these spectra being a mandatory condition of nonradiative energy transfer. He gave the following expression for the rate constant for energy transfer [21]:

$$w_{DA} = \frac{1}{\tau_{0D}} \left(\frac{R_{0DA}}{R_{DA}} \right)^6 \quad (1)$$

in which: τ_{0D} is the average donor fluorescence lifetime in case of acceptor absence, R_{DA} is the distance between the interacting donor and acceptor dipoles, while R_{0DA} is the so-called critical radius (critical distance) for nonradiative energy transfer from an excited donor to unexcited acceptor. The physical sense of this parameter is that it is the distance between the interacting molecules at which the probability of excitation energy transfer equals $\frac{1}{2}$, and its value is determined on the basis of measurements of absorption spectrum of an acceptor and fluorescence one of donor, and on the knowledge of the quantum yield of a donor emission, using the following:

$$R_{0DA} = \left(\frac{9 \ln 10 \langle \kappa_{DA}^2 \rangle \eta_{0D} I_{DA}}{128 \pi^5 n^4 N'} \right)^{\frac{1}{6}} \quad (2)$$

η_{0D} – denotes quantum yield of a donor fluorescence when energy transport is not present, I_{DA} is the overlap integral of the fluorescence spectrum of a donor and the absorption spectrum of acceptor, N' – stands for the number of molecules in 1 mmol, while $\langle \kappa_{DA}^2 \rangle$ – represents the averaged over all configurations value of the orientation factor, which describes the mutual position of the transition dipole moments of an acceptor (in-absorption) and donor (in emission).

The value of the orientation factor of a single donor-acceptor pair is defined as:

$$\kappa_{DA} = \cos \varphi_{DA} - 3 \cos \varphi_D \cos \varphi_A \quad (3)$$

where φ_{DA} denotes the angle between the direction of the transition moment of donor ($\vec{\varepsilon}_D$) and that of acceptor ($\vec{\varepsilon}_A$), φ_D – is the angle between the direction of $\vec{\varepsilon}_D$ and that of \vec{R} , φ_A – the angle between the direction of $\vec{\varepsilon}_A$ and that of \vec{R} (cp. Fig.1)

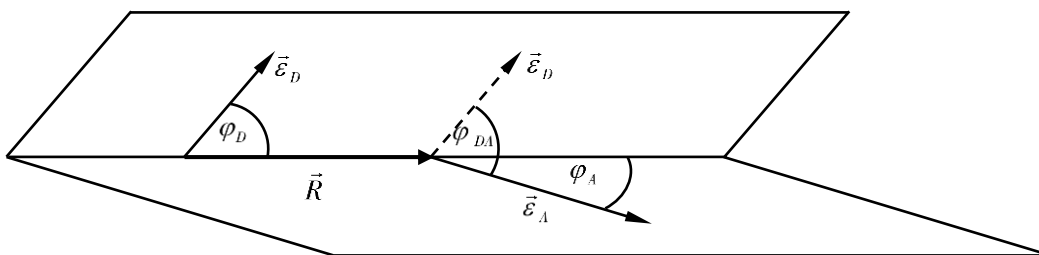


Fig 1. Geometrical configuration of transition dipole moments : acceptor absorption A and donor emission D .

For systems of random distribution of molecules the averaged orientation factor $\langle \kappa^2 \rangle$ depends on τ_{lok}/τ_{rot} , where τ_{lok} – is the mean localization time of excitation on a given molecule whereas τ_{rot} is the rotational relaxation time. The averaged value of the orientation factor changes from $\frac{2}{3}$ [40] for $\tau_{lok}/\tau_{rot} \gg 1$ (fast rotating dipoles) to 0,476 [41] for $\tau_{lok}/\tau_{rot} \ll 1$ (static dipoles). Intermediate cases and the methods to evaluate $\langle \kappa^2 \rangle$ for macroscopically disordered systems have been discussed for example in [42-44].

Natural generalizations of the Förster's model take into account a multi-stage energy migration in a set of donors, which, at a sufficiently high donor concentrations, may precede the energy transfer from a donor to acceptor. In this aspect, two major groups of models have emerged, been developed and function: the so-called hopping model and the diagrammatic model. In the hopping mode, the starting point is a specific system of kinetic differential equations in which fluorophores are divided into groups based on configurations of the nearby unexcited molecules, and excited individuals are categorized into orders, where the light-excited molecules are considered to be of the m -th order if they became excited in the m acts of energy transfer [45].

In the original approach to the hopping model, energy transport processes are treated as the Markov ones. Works based on this model use the formalism of a continuous-time random walk, which was introduced by Montroll for the study of the dispersive nature of energy transport in disordered systems. As further experimental and theoretical work have shown, in many cases the probability of energy return from a certain excited donor molecule to the originally excited donor molecule, after averaging over all configurations, is slightly higher than the probability of transferring this energy to any other molecule from the vicinity of the excited donor.

Therefore, the so-called Huber's function has been introduced, which allows for approximate including of memory effects in the energy transfer processes. This function is a measure of time changes of the conditional probability that if a molecule was excited at a time $t = 0$, it will remain excited at any time $t > 0$ [46]. The modified in this way excitation energy transport model can no longer be treated as the Markovones, and the effect described above, called the intermolecular correlation effect, results in a slight shortening of the effective energy migration range. Intermolecular correlations are usually taken into account if the average time of localization of the excitation energy on a molecule is much shorter than the molecule average rotational relaxation time in the excited state.

The second group of models for radiation-free excitation energy transport, called the Self Consistent Diagrammatic Method (SCDM) model [47, 48], describes a system containing N molecules of donor D

and M traps of the acceptors A excitation energy traps A (acceptors), distributed randomly in an inactive medium of a volume V . The donor molecules are numbered from 1 to N , while the trap molecules are numbered from $N + 1$ to $N + M$. The different configurations of the molecules are described by the molecule position vector $\dagger \mathfrak{R} = (\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{N+M})$. The excitation energy transfer rate constant – $w_{x_i x_j}^{XY}$ – denotes the probability of an excitation transition per unit time from the j -th molecule of the set X to the i -th molecule of the set Y , where X, Y represent the donor D and the acceptor A . Each of the excited molecules of the donor D^* can be deactivated by fluorescence emission, nonradiative transition, nonradiative energy transfer (BTE) from D^* to D ($w_{x_i x_j}^{DD}$) and from D^* to ($w_{x_i x_j}^{DA}$). The dynamics of electronic excitation in the studied system is described by a formula of *master equation* type on $P_{x_i x_j}(t)$, where $P_{x_i x_j}(t)$ denotes the probability density of finding the excitation at time t on the molecule x_i if at the initial time $t = 0$ the molecule x_j was excited, with the initial condition $P_{x_i x_j}(0) = \delta_{ij}$. The information about the system is obtained by averaging this probability over the distribution \mathfrak{R} of the molecules. The Green's function method is used to solve the *master equation*. The Fourier-Laplace transform of the desired Green's function is a series of terms being products of n -elements transition probabilities $w_{x_i x_j}^{XY}$. Summing up all these products ($n \rightarrow \infty$) to obtain the relevant Green's function requires a special computational technique. And the diagrammatic method proved to be the right one here. For this purpose, the individual transition probabilities $w_{x_i x_j}^{XY}$ together with their products are interpreted graphically. The complexity of the diagrammatic series is reduced by a topological reduction procedure. It involves examining the topological structures of diagrammatic series to identify a smaller set of diagrams from which all other diagrams can be generated. Diagrammatic series are renormalized using a procedure removing loops and nodes. To ensure that the behavior of normalizing the total probability to unity is met, the self-consistency procedure is used. The relationship between the theoretical results and the experimentally measured physical quantities is obtained, among others, from the relationship between the fluorescence decay of the initially excited donor – $G^{SD}(t)$ – with the parallel and perpendicular components of the donor fluorescence decay:

$$I_{\parallel}(t) = e^{-\frac{t}{\tau_{0D}}} \left(1 + \frac{4}{5} G^{SD}(t) \right) \quad (4)$$

$$I_{\perp}(t) = e^{-\frac{t}{\tau_{0D}}} \left(1 - \frac{2}{5} G^{SD}(t) \right) \quad (5)$$

As a result, an expression for the experimentally measurable decay of emission anisotropy is obtained:

$$r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)} \quad (6)$$

which provides valuable information on the rotational dynamics and molecular interactions of fluorophores. The SCDM model in the so-called three-body approximation leads to a decay function which shape depends not only on the concentration, but also on the quotient of the critical radii for energy transfer and migration, which is interpreted as a manifestation of a process that is not a stochastic Markovian process (correlations are therefore also taken into account) [48].

An interesting practical aspect of the developed theories of energy transport in disordered systems is that despite significant differences in the construction of systems of differential equations describing these stochastic processes in both groups of models, as well as in different methods of solving them and different approximations applied, the results characterize the time and concentration courses of the luminescent characteristics of the system. Two-compound donor-acceptor systems appear to be very similar in both cases and usually consistent with the results of numerous experiments.

Further improvement in both groups of models was taking into account an extra channel of excitation energy migration, which may be the reverse energy transfer from an excited acceptor to the set of donors [25]. First, an intuitively simple but not very accurate development of the hopping model emerged in which expressions for the concentration waveforms of the quantum yield and emission anisotropy were uncovered. In this model, the origin of delivering not very correct results, especially with regard to emission anisotropy, was the assumption made that the excitation energy is not transferred from a set of acceptors to those donor molecules that were initially excited by the excitation light beam, i.e. those ones that mostly contribute to the emission anisotropy. In a more accurate, diagrammatic model, this assumption was not introduced.

A necessary condition for this process to occur is an overlap of the fluorescence spectrum of an acceptor with the absorption one of donor, which is the case in donor-acceptor systems with spectrally close excited singlet states of donors and acceptors, such as, for example, chlorophyll systems, range of ionic forms of some dyes (e.g. rhodamine B), fractions of luminescent molecules in systems with heterogeneous broadening, as well as monomers and fluorescent aggregates of flavomononucleotide, rhodamines, carbocyanins, Nile Red, etc. The rate constant for this process is similar in nature to that for a simple transfer or energy migration, the efficiency, however, of the process is lower, due to a smaller overlap of the corresponding spectra.

Considering the reverse energy transfer in the diagrammatic model appeared to be much more complicated, and the results themselves, however very accurate, difficult to exploit from a practical point of view. Success in the description of experiments was achieved here only by introducing a theoretical method of summing infinite series, containing configuration-averaged Green's functions and utilizing the fractal structure of multigraphs [25].

It seems that further progress in building analytical models taking into account simple transfer, energy migration and reverse energy transfer in systems with a larger number of components, partially ordered systems, low-dimensional structures and so on, is very doubtful due to the rapidly growing complexity of such systems. Moreover, the results of even the most developed theories of energy transfer in three-dimensional disordered systems cannot be applied to the above-mentioned cases.

For example, no expression for emission anisotropy has been derived in uniaxially oriented polymers until now in the presence of excitation energy migration and transfer. In such systems the distribution of dipole moments of fluorophores which participate in excitation energy is no longer random but evident change in the angular distribution of transition dipole moments of interacting molecules takes place which leads to mutual strong correlations. As a result the energy transfer between such fluorophores exhibits often strongly preserved emission anisotropy even after several acts of transfer,

whereas in disordered systems the contribution of acceptors to emission anisotropy is negligible. Similarly, the analyses of excitation transport its trapping in limited volume systems and containing relatively small number of fluorophores like nanoparticles labelled with donors and acceptors at the surface are far from being completed.

Monte Carlo Simulations

The Monte Carlo simulation method has now become a recognized tool in many fields of science. The reasons for using Monte Carlo simulations are numerous [49, 50], and the main ones are:

- it allows the study of systems for which there is no precise analytical description,
- it enables analysis of emergent behavior and properties of highly complex systems (e.g., molecular models, biological systems, social networks and financial markets),
- it delivers data that can be used to verify approximate theories (comparing simulation results with those obtained from simpler mathematical models allows one to assess the accuracy of these approximations),
- it allows comparison of the created models with the experimental data (this is an important verification tool that lets one to assess how well a theoretical model reflects the actual behavior of the tested system),
- it enables the development of criteria for assessing the accuracy of model selection (this allows for a more objective approach of justifying the effectiveness of various theories or models in describing considered physical systems).

Of course, the Monte Carlo simulations are an important research tool in physics. They bridge the gap between theory, analytical description and experiment. For example, they make it possible to calculate the values of those quantities characterizing complex physical systems that are difficult to obtain from experiments. In the study of the excitation energy transport phenomena, there is a range of such important quantities that can be calculated using Monte Carlo simulations, which are not possible to be measured directly. These quantities include, for example:

- Average excitation energy localization time on a molecule and the average number of excitation energy jumps.
Localization time is the average time within which the excitation energy remains on a single donor in the process of its travel in a system. This quantity is in a close relation to the average fluorescence lifetime: $\tau_{lok} = \tau_{0D}/(n-1)$, where n is the number of the excitation energy jumps during its migration in a set of donors in a given donor-acceptor molecular system, and τ_{0D} is the average lifetime of fluorescence in the absence of acceptors
- Mean square shift of the excitation energy in the process of energy migration.
This quantity makes it possible to assess how far, on average, the excitation energy travels during its transport from the site of original excitation. It can be particularly interesting to compare the value of this quantity with the size of nanostructures on which energy donors and acceptors reside.
- Average orientation factor.
It determines the average orientation of molecules in the examined system. This quantity can affect both the efficiency and the extent of the energy transfer.
- Emission intensity decay of the initially excited molecules.
This quantity can be directly related to the emission anisotropy of in disordered systems.

- Contribution to the emission anisotropy of the molecules excited initially and excited secondarily by energy transfer.

Much higher than zero, for example, value of the anisotropy of emission of the molecules excited by energy transfer (secondarily excited) delivers useful information about certain average spatial ordering of the transition moments of the interacting molecules.

Basic parameters used in the Monte–Carlo simulation to investigate excitation energy transfer are: parameters characterizing the geometry of the tested system, concentrations of acceptors and donors, C_A, C_D , respectively, critical radii for the energy transfer for homotransfer (migration) between donors, donor – acceptor transfer and homotransfer between acceptors: $R_0^{DD}, R_0^{DA}, R_0^{AD}, R_0^{AA}$, respectively, and the number of fluorophores (N donors and M acceptors). Using a uniform pseudorandom numbers generator the molecules are randomly distributed randomly or in accordance with the geometry of the system and the spatial orientations of transition dipole moments in the absorption and emission are generated ($\vec{\varepsilon}_j^A, \vec{\varepsilon}_j^E$). Let us denote by φ_j the angle between the direction of transition dipole moment in the absorption $\vec{\varepsilon}_j^A$ projected on the surface O_{xy} and the axis x . ϑ_j is the angle between transition moment $\vec{\varepsilon}_j^A$ and the chosen axis z , and β denotes the angle between transition dipole moments in the absorption and the emission. Both angles describe by the uniform distribution of transition moments on a unit sphere, i.e., $\cos \vartheta_j \in [-1, 1]$ and φ_j is from the interval $[0, 2\pi]$. The angle β for different fluorophores can vary from 0 to 90 degrees. The described geometry of the system is visualized in Fig. 2.

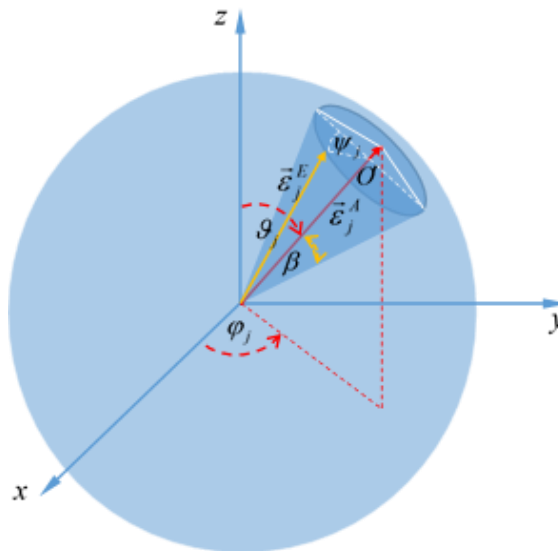


Figure 2. The geometry of the system.

The Förster rate constant for energy transfer between the j -th and i -th molecules is determined based on formula (1):

$$w_{x_i x_j} = \frac{\kappa_{ij}^2}{\tau_0} \left(\frac{R_0^{XY}}{r_{ij}} \right)^6 \quad X, Y \in \{D, A\} \quad (7)$$

where: r_{ij} is the distance between the i -th and j -th molecule, κ_{ij}^2 is the real orientation factor for a given molecular pair. For the purpose of simulation the orientation factor, κ_{ij}^2 , is defined as:

$$\kappa_{ij}^2 = [\vec{\varepsilon}_i^E \cdot \vec{\varepsilon}_j^A - 3(\vec{\varepsilon}_i^E \cdot \vec{r}_{ij}) \cdot (\vec{\varepsilon}_j^A \cdot \vec{r}_{ij})]^2$$

Including a real value of the orientation factor κ_{ij}^2 into the transfer rate (eq. 7) allows for investigations of the influence of a mutual orientation of transition moments on excitation energy transfer.

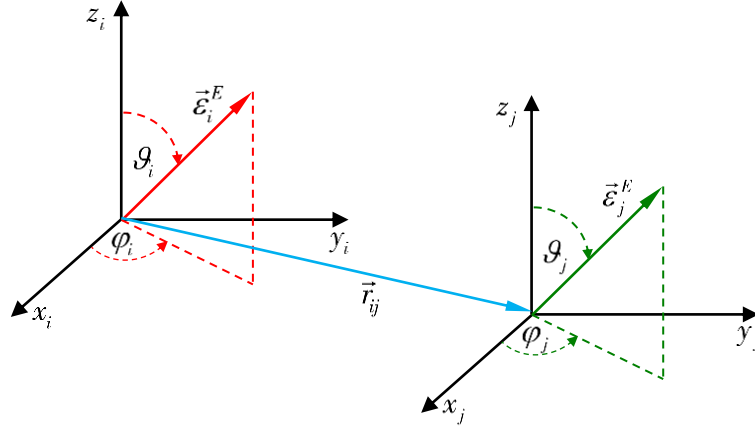


Figure 3. The concept of κ_{ij} .

The dynamics of the simulated system, i.e. conditional probability that an excitation is found on i -th molecule at time t , $P_{x_i x_j}(t)$, while it was at time $t = 0$ on j -th molecule, for the fixed molecular configuration, obeys the following *master equation*:

$$\begin{aligned} \frac{dP_{x_i x_j}(t)}{dt} = & -\frac{1}{\tau_{0D}} P_{x_i x_j}(t) + \sum_{k=1, k \neq i}^N w_{x_i x_k}^{DD} P_{x_k x_j}(t) - \sum_{k=1, k \neq i}^N w_{x_k x_i}^{DD} P_{x_i x_j}(t) + \\ & - \sum_{k=N+1}^{N+M} w_{x_k x_i}^{DA} P_{x_i x_j}(t) + \sum_{k=N+1}^{N+M} w_{x_i x_k}^{AD} P_{x_k x_j}(t) \end{aligned} \quad (8)$$

$$N + 1 \leq i \leq N + M$$

$$\begin{aligned} \frac{dP_{x_i x_j}(t)}{dt} = & -\frac{1}{\tau_{0A}} P_{x_i x_j}(t) + \sum_{k=1}^N w_{x_i x_k}^{DA} P_{x_k x_j}(t) - \sum_{k=1}^N w_{x_k x_i}^{AD} P_{x_i x_j}(t) + \\ & + \sum_{k=N+1, k \neq i}^{N+M} w_{x_i x_k}^{AA} P_{x_k x_j}(t) - \sum_{k=N+1, k \neq i}^{N+M} w_{x_k x_i}^{AA} P_{x_i x_j}(t) \end{aligned} \quad (9)$$

$$N + 1 \leq i \leq N + M$$

with the initial condition $P_{x_i x_j}(0) \equiv \delta_{ij}$, where δ_{ij} is the Kronecker delta.

The step-by-step Monte Carlo simulation method used in the publications is based on the use of a pseudorandom number generator to cyclically formulate answers to two questions:

- when one of the previously determined processes takes place in the simulated system,
- what type of a process it is.

Molecules originally excited are selected in accordance to the $\cos^2 \mathcal{G}_j$ probability distribution, what means, that with the largest probability those molecules become excited which have the transition moments parallel to the direction of the electric vector of the excitation light. Hence, a random number r_j from uniform distribution on interval $[0, 1]$ is generated. If the following inequality is fulfilled:

$$\cos^2 \mathcal{G}_j \geq r_j \quad (11)$$

the j -th molecule becomes excited. The molecules breaking this inequality are rejected from the set of originally excited molecules.

In the Monte–Carlo simulation the deactivation of j -th molecule may occur through the following processes:

For donors:

P_1 : photon emission or nonradiative energy conversion, with the rate $1/\tau_{0D}$

P_2 : energy migration with the transfer rate $w_{x_i x_j}^{DD}$,

P_3 : nonradiative energy transfer from the excited donor to an acceptor, with the transfer rate $w_{x_i x_j}^{DA}$.

For acceptors:

P'_1 : photon emission or nonradiative energy conversion, with the rate $1/\tau_{0A}$

P'_2 : energy migration with the transfer rate $w_{x_i x_j}^{AA}$,

P'_3 : reversible transfer from acceptor to donor with the transfer rate $w_{x_i x_j}^{AD}$,

Next, for the j -th excited donor molecule the values of the following total transfer rates are calculated:

$$c_{1j} = \frac{1}{\tau_{0D}} \quad c_{2j} = \sum_{i=1, i \neq j}^N w_{x_i x_j}^{DD} \quad c_{3j} = \sum_{i=N+1}^{N+M} w_{x_i x_j}^{DA} \quad c_j = c_{1j} + c_{2j} + c_{3j} \quad (12)$$

and for the i -th excited acceptor molecule:

$$c'_{1i} = \frac{1}{\tau_{0A}} \quad c'_{2i} = \sum_{j=N+1, j \neq i}^{N+M} w_{x_j x_i}^{AA} \quad c'_{3j} = \sum_{j=1}^N w_{x_j x_i}^{AD} \quad c'_i = c'_{1i} + c'_{2i} + c'_{3i} \quad (13)$$

The time at which any of the investigated processes occurs is calculated by inverting the distribution function of the probability, $p_j(t, P_k) dt$, that if at time t the j -th molecule is excited, then the process P_k appears in the time interval $(t, t + dt)$:

$$p_j(t) = \sum_{k=1}^3 P_j(t, P_k) = c_j \exp(-c_j t) \quad (14)$$

Generating a random number r_{1j} from the interval $[0,1]$ the time at which any process takes place is obtained by inverting the distribution function $p_j(t)$:

$$\int_0^{t_j} p_j(t) dt = r_{1j} \quad t_j = -\frac{1}{c_j} \ln(1-r_{1j}) \quad (15)$$

Next, it is determined which process took place at time t_j . By generating next random number, r_{2j} , such a value of index k can be found for which the following inequality is satisfied:

$$\sum_{i=1}^{k-1} c_{ij} < r_{2j} c_j \leq \sum_{i=1}^k c_{ij} \quad k = 1,2,3 \quad (16)$$

Depending on the value of the k index, the appropriate process takes place:

- for $k = 1$ the activated molecule is quenched by a photon emission or nonradiative excitation energy conversion. This process ends the current simulation run.
- for $k = 2$ or $k = 3$ the energy migration or energy transfer process takes place, and it is necessary to determine which molecule is activated next. For this reason the third random number, r_{3j} is generated and the value of index n is found which fulfils one of the inequalities:

$$\sum_{i=1}^{n-1} w_{x_i x_j}^{DD} < r_{3j} c_{2j} \leq \sum_{i=1}^n w_{x_i x_j}^{DD} \quad k = 2, n \leq N \quad (17)$$

or

$$\sum_{i=N+1}^{n-1} w_{x_i x_j}^{DA} < r_{3j} c_{3j} \leq \sum_{i=N+1}^n w_{x_i x_j}^{DA} \quad k = 3, n > N \quad (18)$$

where n is the number of next activated donor or acceptor.

If the donor ($k=2$) has been excited, then knowing which donor molecule is currently excited, the total values of the rate constants for it are calculated and it is again determined at what next moment the appropriate physical process will occur (deactivating the excitation) and what this process will be.

When an acceptor molecule ($k=3$) is excited as a result of energy transfer from the donor, one of the processes P'_1 (photon emission), P'_2 (energy migration in acceptor ensemble) or P'_2 (reversible energy transfer to donor) occurs by generating another random number r_{4j} and finding the value of the index k' , for which the following inequality is satisfied:

$$\sum_{l=1}^{k'-1} c'_{li} < r_{4j} c'_i \leq \sum_{l=1}^{k'} c'_{li} \quad k' = 1,2,3 \quad (19)$$

If $k=1$, then the activated acceptor molecule is quenched by a photon emission or nonradiative excitation energy conversion and it means that this pass of simulation is finished. If $k=2$ or $k=3$ it is necessary to determine to which molecule: donor or acceptor the excitation energy was transferred. For this

reason the third random number, r_{5j} is generated and the value of index m is found which fulfils one of the inequalities:

$$\sum_{l=N+1}^{m-1} w_{x_l x_l}^{AA} < r_{5j} c'_{2j} \leq \sum_{l=N+1}^m w_{x_l x_l}^{AA} \quad m > N \quad (20)$$

or

$$\sum_{l=1}^{m-1} w_{x_l x_l}^{AD} < r_{5j} c'_{3j} \leq \sum_{l=1}^m w_{x_l x_l}^{AD} \quad m \leq N \quad (21)$$

Having known which molecule (donor or acceptor) is currently excited, total values of rate constants are for it calculated. Next, it is established at what time moment a physical process of choice takes place and what a process it is. This procedure is continued until emission of photon occurs, which completes the simulation run. Next, described simulation run is repeated for a new special and angular configuration. Having known angular coordinates and the time moment at which molecule emitted a photon we calculate the decays of respective components of emitted light intensity:

$$I_z(t) = I_0 \cos^2 \vartheta_j(t) \quad (22)$$

$$I_x(t) = I_0 \sin^2 \vartheta_j(t) \cos^2 \varphi_j \quad (23)$$

$$I_y(t) = I_0 \sin^2 \vartheta_j(t) \sin^2 \varphi_j \quad (24)$$

In Monte Carlo simulations emission anisotropy as a function of time can be obtained by three independent ways (in order to control the correctness of the algorithm). Subsequent random number r_j from the interval $[0, 1]$ is generated and if $\cos^2 \vartheta_j \geq r_j$, then it means that the emitted by excited molecule photon has polarization along O_z axis (I_{\parallel} component). In the opposite case photon has I_{\perp} polarization (the algorithm resembles that of photon counting method). Next, the following formula is applied:

$$r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)}$$

To verify the results of Monte-Carlo simulation it is necessary to use the general definition of emission anisotropy:

$$r(t) = \frac{I_z(t) - I_y(t)}{I_x(t) + I_y(t) + I_z(t)} \quad (25)$$

as well as an equivalent formula for systems exhibiting axial symmetry (if we deal for example with uniaxially oriented polymer film):

$$r(t) = \frac{3}{2} \cos^2 \vartheta_i(t) - \frac{1}{2} \quad (26)$$

The results obtained based on these three formulas should be approximately the same evidencing the correctness of the simulation algorithm and its implementation.

Relative donor fluorescence quantum yield can be obtained as a ratio of the number of simulation cycles terminated with photon emission to the number of all simulation cycles performed.

Normalized decay in the form of a histogram is obtained from the formula:

$$I(t_k) = 1 - \frac{\sum_{j=1}^k n_j}{\sum_{j=1}^{k_{\max}} n_j} \quad (27)$$

where: $t_k = \left(\frac{k}{k_{\max}}\right)t$, $k = 1, \dots, k_{\max}$, n_k – denotes the number of photons in the k -th channel, k_{\max} is the total number of all photons.

To minimize the inaccuracies due to the finite number of molecules and boundary effects in studies involving uniaxially oriented polymers, periodic boundary conditions combined with the principle of closest image of a given molecule are incorporated into the Monte-Carlo simulation. The periodic boundary conditions are obtained by duplicating the base cell in all directions. This minimizes the impact of edge effects on the simulation result.

In order to obtain reliable statistics describing the investigated phenomena, it is necessary during the simulations to follow a sufficiently large number of steps corresponding to specific processes. The convergence and stability of the results can be assessed by observing how the subsequent trials affect the average values. In the simulations performed, the results were averaged after a certain number of trials in such a way that the variance of the simulated observations was small enough, for example 0.1%.

As I mentioned, the analysis of the multi-step energy migration process in some systems, for example, in ordered PVA films containing fluorophores, is currently possible only through computer simulations. Modeling certain quantities for such a system, such as: the decay of fluorescence emission anisotropy, is very time-consuming, even on modern multicore computers, when the traditional step-by-step Monte Carlo modelling algorithm is utilized. This problem has been solved by the development of a new hybrid Monte Carlo simulation algorithm, which allows significantly faster, up to several hundred times, calculations [51].

The starting point of the hybrid Monte Carlo simulations is a formula of the master equation type, describing the dynamics of the simulated system. To solve it, the Green's function method is applied. The Green's function is expressed using the eigenvalues and eigenvectors of the transition matrix \mathbf{W} , formed from the rate constants of the energy transfer between molecules. During a hybrid Monte Carlo simulation, for a given set of parameters characterizing the geometry and energy transfer in the system under study, the molecules are distributed either randomly or according to the assumed model. For a given configuration of molecules, first the rate constants that are elements of the \mathbf{W} matrix are calculated, and subsequently also the eigenvectors and eigenvalues, by which the simulated observables, such as anisotropy decay, are expressed. The final results are obtained by averaging over a sufficiently large number of spatial and angular configurations of the simulated molecules. The convergence of this Monte Carlo algorithm is much faster than of the step-by-step algorithm, especially for longer times, e.g. of $u \gg 3 \tau_{0D}$ order.

The starting point of the hybrid Monte Carlo simulation is a formula of the *master equation* type, describing the dynamics of the system under study:

$$\frac{d\mathbf{P}(\mathfrak{R}, t)}{dt} = \mathbf{W} \circ \mathbf{P}(\mathfrak{R}, t) \quad (28)$$

The formal solution to the above equation is:

$$\mathbf{P}(\mathfrak{R}, t) = \exp(\mathbf{W}t) \circ \mathbf{P}(\mathfrak{R}, t = 0) \quad (29)$$

And the Green's function describing the donor decay is of the following general form:

$$G^D(t) = \left\langle \frac{1}{\tau_{0D}} \sum_{i=1}^N \sum_{j=1}^{N+M} g_{ij}(t) P_{x_i, x_j}(0) \right\rangle_{\mathfrak{R}} \quad (30)$$

where the symbol $\langle \cdot \rangle_{\mathfrak{R}}$ means averaging over all possible spatial and angular configurations of molecules. After using the initial condition and the explicit form of the matrix elements of the full Green's function, one gets:

$$G^D(t) = \frac{1}{N\tau_{0D}} \left\langle \sum_{i=1}^N \sum_{j=1}^N (\exp(\mathbf{W}t))_{ij} \right\rangle_{\mathfrak{R}} \quad (31)$$

The Green's function expressed by the eigenvalues and eigenvectors of the transition matrix \mathbf{W} is given by:

$$G^D(t) = \frac{1}{N\tau_{0D}} \left\langle \sum_{i=1}^N \sum_{j=1}^N \sum_{k=1}^{N+M} \mathbf{Z}_{ik} \mathbf{Z}_{kj}^{-1} \exp(-\lambda_k t) \right\rangle_{\mathfrak{R}} \quad (32)$$

The emission anisotropy decay is calculated from definition formula (6):

$$r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)}$$

where the components of light intensity emitted by the investigated object are as follows:

$$I_{\parallel}(t) \propto \frac{1}{N} \left\langle \sum_{i=1}^N \cos^2 \vartheta_i(t) \sum_{j=1}^N (\exp(\mathbf{W}t))_{ij} \cos^2 \vartheta_j(0) \right\rangle_{\mathfrak{R}} \quad (33)$$

$$I_{\perp}(t) \propto \frac{1}{N} \left\langle \sum_{i=1}^N \sin^2 \vartheta_i(t) \cos^2 \varphi_i(t) \sum_{j=1}^N (\exp(\mathbf{W}t))_{ij} \cos^2 \vartheta_j(0) \right\rangle_{\mathfrak{R}} \quad (34)$$

DISCUSSION OF WORKS CONSTITUTING THE HABILITATION CYCLE

Energy transport in a two-compound disordered system in the form of a polymer and a thin-film hybrid matrix

As I have already shown in an earlier part of the Summary of Professional Accomplishments, the theoretical description of the excitation energy transport in two-compound disordered systems has reached a high level of development. In general, it takes into account not only the transfer of energy from a donor to acceptor or the multi-stage energy migrations in a set of donors, but also the effects of the reverse energy transfer from an acceptor to donor, which may be preceded by energy migration in the set of acceptors. However, the designing the experiments and analyzing experimental systems in which such a wide range of processes takes place is a nontrivial task, yet it is worth the efforts as they will result in the possibility of a correct description such quite complex system as well as the obtaining valuable information about the properties of the energy transfer itself. I analyzed in this context a disordered system in which I investigated the concentration dependence of the quantum yield and the emission anisotropy of rhodamine S in thin films of polyvinyl alcohol (**paper H1**). It turned out that with the increasing concentration, a common phenomenon occurs of aggregates formation (dimers in the considered situation) in the ground state in the system, which is indicated by characteristic changes in the absorption spectrum profile (**Fig. 1ab in paper H1**). Numerical analysis of the family of absorption spectra revealed a dimer absorption spectrum consisting of the H band, located on the short-wavelengths side of the monomer band maximum, and the J band, located on the long-wavelengths side of the monomer band. Because of a partial spectral overlap between the monomers fluorescence and the dimers absorption spectra, as well as the absorption and fluorescence ones of the monomers themselves, we deal in a good approximation with a two-compound system in which, already at a first glance, donors role is played by the rhodamine monomers, and the role of acceptors is played by the rhodamine dimers, and the possible processes are energy transfers from monomers to dimers, which may be preceded by energy migration in a set of monomers. The formation of higher order aggregates could have been neglected in the studied concentrations range considering the conservation of the isozbestic points in the absorption spectra and the performed detailed numerical analysis of the whole family of the absorption spectra. It further comes out that the fluorescence spectra profiles also show changes with increasing concentration, which manifest themselves in appearance of a long-wavelength emission band, and taking into account the very low optical density of the samples (thin films), these changes do not originate from artifacts in the form of secondary effects, but are related to the possibility of emission by aggregates of not very strong fluorescence from the J-band. Spectral overlap of the aggregate fluorescence with the monomer absorption spectrum (**Fig. 1 ab and Table 2 in paper H1**) uncovers also other channels of the excitation energy migration, in the form of a reverse transfer from dimers to monomers, which may be preceded by energy migration in a set of dimers. Such fluorescent aggregates with some ability to a reverse energy transfer to a set of monomers are sometimes called imperfect excitation energy traps. The values of the critical radii listed in Table 2 clearly show that the reverse energy transfer is indeed a distinctly weaker phenomenon than the transfer from donors to acceptors, however, as indicated by the performed analysis, it cannot be indiscriminately neglected.

The paper H1 (**Fig. 2ab and 3ab**) presents the results of a concentration quenching and concentration depolarization of fluorescence. The analysis of the experimental results was carried out based on the

Monte-Carlo simulations and two models of energy transfer: the one that includes the reverse energy transfer and a simpler one, that neglecting this effect. And the following conclusions could be drawn:

- a) The model neglecting the reverse energy transfer does not describe correctly the experimental data, especially in the high concentrations range. It predicts stronger concentration quenching of fluorescence than it comes from experimental data and clearly underestimates the emission anisotropy in the high concentrations range. In particular, **Fig.3a (paper H1)** does not show at all the effect of fluorescence repolarization, characteristic for systems with perfect traps.
- b) The hopping model, accounting for the reverse energy transfer, describes very well the phenomenon of concentration quenching in the system over the entire concentrations range, and the description of fluorescence concentration depolarization can be considered qualitatively satisfactory and much better than that provided by a simpler model that neglects the reverse energy transfer.
- c) The Monte-Carlo simulations of both phenomena appear, in each case, to deliver good description of the experimental data, and across the full range of concentrations (with a quality close to predictions of the theoretical model that takes into account the reverse energy transfer).

The performed analysis made it possible to estimate the quantum yield of dimers, which turned out to be quite low, 0.03 at 293 K and 0.015 at 333 K, respectively. At higher temperatures, due to the temperature quenching of fluorescence and lower concentration of dimers in the system, the reverse energy transfer process is less efficient, which is reflected in a smaller spread of theoretical curves obtained for both models. The agreement between the predictions of the model taking into account the reverse energy transfer and the results of the Monte-Carlo simulations as well as generally good description of the experimental data indicate that this effect cannot be neglected during analysis, even if it is only a relatively weak one.

The executed analysis can constitute a kind of reference for evaluating the behavior of other specific fluorinating systems, e.g., aggregating hybrid porous systems, uniaxially oriented polymers or biological membranes containing fluorophores in high concentration. Further on, the **paper H4** will be discussed, related, among other things, to energy transport processes in a hybrid thin-film porous matrix doped with rhodamine 6G molecules.

Luminescent hybrid materials play an important role in the design and manufacturing of functional materials, biosensors, nanomedicine, implantology, photocatalysis [52, 53]. They are promising carriers of biologically and medically active substances. One of the modern hybrid materials type, possessing the desired optical and mechanical characteristics in a long timescale, are those obtained by low-temperature sol-gel technology. The method is simple, allows to obtain reproducible, durable materials, enabling incorporation of numerous molecules of different application importance [54, 55].

In these heterogeneous, nanoscale and microscale, materials, fluorophores due to preferential solvation can locate mainly in the pores of a given matrix. The porosity of the structure (density of pores distribution) can be influenced by appropriate selection of sol-gel process components, reaction conditions and choice of catalysts.

Because of the microscopically heterogeneous structure of the matrix, there is a significant increase in the local concentration of dye molecules in certain areas of the matrix and a decrease in others comparing to the predicted average concentration resulting from the number of molecules initially dissolved and the final volume of the sample.

Indeed, during my studies on the incorporation of various organic dyes into inorganic thin films based on SiO₂, TiO₂ and others, it appeared that despite the relatively low molar concentrations of dyes I used, the spectroscopic characteristics of the studied systems did not correspond to the spectra of relevant molecules in monomeric form, known from solutions, and showed the characteristics of partially aggregated systems. I observed additional bands in the absorption or fluorescence excitation spectra corresponding to the changes typical for aggregates, but visible in solutions or polymers at much higher concentrations. Similarly, I observed also a shortening of the average fluorescence lifetime and a deviation of the fluorescence intensity decay curve from a uni-exponential function. The sum of these preliminary observations and results in the context of the porosity of the investigated structures led me to plan a range of experiments to assess what average local concentrations can be expected in such materials under given experimental conditions, and how such locally increased concentrations translate into processes of energy transfer and energy trapping. Estimating the average local concentrations of luminophores in such heterogeneous systems is, in my opinion, important in describing the optical properties of such materials, together with the processes taking place in them and their subsequent applications. As it turned out, the phenomenon of nonradiative energy transfer is very well suited to carry out this kind of such estimation. A method to determine the average local concentration of a dye is described in **papers H3 and H4**. In the **paper H3**, I proposed for the first time and tested a method for determining the average local concentration of a dye in a donor-acceptor binary system. The motivation for performing the study, at a first place in the donor-acceptor system, and only then in the systems with present aggregation, was to obtain at the beginning a system as simple as possible for later analysis with the possibility of maintaining better control over the resulting donor and acceptor concentrations.

For the study, I chose a pair of rhodamines: rhodamine 110 as the donor of the electronic excitation energy and rhodamine 101 as the acceptor, which were incorporated into two types of thin matrices obtained on the basis of SiO₂. Both of these dyes aggregate only at high molar concentrations in the investigated environments. Basic studies of the absorption and fluorescence spectra have shown (**Fig. 1 in paper H3**) a partial overlap of a donor emission and acceptor absorption spectra, thus in this system the conditions necessary for the occurrence of a donor-acceptor energy transfer as well as multistep donor-donor migration are fulfilled. At the same time, the reverse energy transfer can be neglected because of negligible overlap of the emission spectrum of rhodamine 101 and the absorption one of rhodamine 110. The experiments were arranged in such a way that the molar concentration of the donor $C_D = 5 \cdot 10^{-5}$ mol/l was fixed and identical for all the samples, while the acceptor concentration varied from $C_A = 5 \cdot 10^{-5}$ mol/l to $C_A = 2 \cdot 10^{-3}$ mol/l.

Based on the spectroscopic measurements, I determined the values of the critical radii and concentrations, necessary to describe the energy transfer and possibly also the energy migration in the examined system ($R_{0DD} = 46$ Å, $R_{0DA} = 56$ Å; $C_{0DD} = 4.1 \cdot 10^{-3}$ mol/l i $C_{0DA} = 3 \cdot 10^{-3}$ mol/l).

The results of the time evolution measurements of the fluorescence spectra showed (**Fig. 3ab. and Table 1 in paper H3**) that in case of a methylated SiO_2 matrix (Me-SiO_2) the energy transfer is more efficient compared to the SiO_2 matrix. Considering the same critical parameter values for both matrices and the same donor and acceptor concentrations in both matrices, one would have to attribute this effect to a higher local acceptor concentration in the Me-SiO_2 . The acceleration of the fluorescence decay and shortening of the average donor lifetimes, observed based on the experimental results, is indeed stronger for the Me-SiO_2 matrix. The proposed by me method for determining the average local concentrations of dyes in porous sol-gel matrices exploits the Monte Carlo simulations of the excitation energy transfer processes. This analysis involves looking for the best match between the results of the Monte Carlo simulations of fluorescence intensity decays in the presence of energy transfer to the experimental fluorescence intensity decays, with the matching parameter in each case being the concentration of the excitation energy donors and acceptor (**Figure 4 in paper H3**). So as to increase the reliability of the fit, the donor concentration, which should be the same in each sample, was assumed to be identical for each simulation run. With such imposed constraints, a good and formally and physically unambiguous description of the experimental results was obtained.

As a result of the analysis, the average local concentrations of the donor and acceptor in the matrices studied were determined (**Table 2 in paper H3**), which appeared to be about one order of magnitude higher than it would take place in case of a homogeneous distribution of the fluorophores in the matrix. At the same time, in **Fig.3** in the same paper, it can be seen how far with such an unjustified assumption of a homogeneous distribution the results of the Monte-Carlo simulations would deviate from the experimental data.

As I described earlier, the excitation energy transfer accompanies also aggregation processes in concentrated systems, therefore I applied the method of determining the local concentrations of a dye, described and tested in work H3, after relevant modifications, to determine the average local concentrations of fluorescent aggregates of rhodamine 6G (**paper H4**). In this case, the role of the energy donor was played by the rhodamine 6G monomer, and the role of the energy acceptor was played by aggregates of this molecule. Absorption and fluorescence spectra profiles obtained for low and high concentrations of rhodamine 6G based on SiO_2 matrices with an acidic catalyst (as opposed to the alkaline one used in paper H3) are significantly different (**Fig.1ab in paper H4**). For a high concentrations of the molecule in silica nanolayers, I observed the appearance of a distinct band at the short-wavelength side of the absorption spectrum (at about 500 nm), as well as a broadening of the fluorescence spectra and a shift of their maxima toward longer wavelengths. The occurrence of two absorption bands of rhodamine 6G aggregate with similar positions and band shapes as in other media supports the assumption that these are dimers.

After analyzing the family of absorption spectra using our own software, the absorption spectra of dimers were obtained, consisting of the H band, located on the short wavelengths side of the maximum of the monomer band, and the J band, respectively, located on the long wavelengths side. Fig. 1ab (**paper H4**) shows common wavelength ranges for the monomer fluorescence and dimer absorption spectra, as well as the dimer emission and monomer absorption spectra, which allows us to conclude that in the considered systems both direct (from monomer to the aggregate) and reverse (from aggregate to monomer) excitation energy transfer can take place.

The results of the time-resolved spectroscopy studies also confirmed the deviations from the single-component nature of system with increasing dye concentration in both matrices (**Fig. 3 in work H4**).

In order to determine concentrations of rhodamine 6G aggregates, in the **paper H4**, similarly to the case of donor-acceptor systems, a comparison of the experimentally obtained fluorescence intensity decays was made with the results of the results from relevant Monte Carlo simulations, in which the algorithm was modify to include the process of a excitation energy reverse transfer. Presuming the concentration of monomers and aggregates in a given matrix to be the best fit parameters, average local values of the concentrations of aggregates and monomers were obtained.

Figure 4 from **paper H4** shows the key results of this work, along with the concentration values for which the best fit was obtained between the Monte Carlo simulation results and the experimental data. As the concentration of the local dye in the matrix increases, a strong acceleration of the fluorescence intensity decay of the monomer and a shortening of the average lifetime of its fluorescence due to the stronger and stronger energy trapping by the dimers. It is worth paying attention to the case of the most dynamically decaying fluorescence intensity curves. Of the visible pair of continuous curves, only one correctly describes the experimental results. And the curves that rightly describe the experimental results for both matrices were created taking into account in the simulation the reverse energy transfer. Neglecting this effect results in too fast emission intensity decays when compared to the experimental data.

The method I developed and experimentally verified, for determining the average local concentrations in nanolayers (**papers H3 and H4**) showed, on the example of a donor-acceptor and monomer-fluorescent aggregate systems, that the concentrations of acceptor molecules or aggregates can be in porous systems several times higher than in the case of a homogeneous distribution of molecules in a matrix.

In summary, the scientific achievement presented in the papers H1, H3 and H4 comprises creating a coherent description of the nonradiative energy transport in thin-film hybrid systems (papers H3 and H4) and identifying the differences in this description while compared to a two-compound disordered system (paper H1). In particular, I developed and tested a method utilizing the Monte Carlo simulations of the excitation energy transfer processes to analyze fluorescence intensity decays, allowing the determination of the average local concentrations of fluorophores and aggregates in thin-layer hybrid porous materials.

In addition to the research on nonradiative energy transport, I also co-worked in the study of aggregation processes in new highly luminescent hybrid materials formed on the basis of titanium dioxide, zirconium dioxide, and silicon dioxide, containing efficient organic fluorophores [56, 57]. In these studies, among other things, the properties of the materials manufactured in the form of nanolayers were compared with those of materials fabricated as bulk xerogels. Big differences in the structure and topography of the tested materials in the form of nanolayers and bulk samples result in significant differences in the observed spectroscopic characteristics. It was found that in case of bulk samples, the aggregation of dye molecules is much stronger than in the case of nanolayer materials. Moreover, the volume samples require special attention due to the possibility of secondary effects appearance, especially when photophysical processes dependent on the fluorophore concentration are studied. Finally, it was possible to explain the controversies appearing in the scientific literature regarding the

role of aggregation and secondary effects in hybrid materials. These works, however, are not included in my habilitation cycle.

As I have shown in the works discussed so far, the quantitative description of energy transfer in systems such as porous nanolayers is more difficult than in disordered systems.

Another example of an interesting and important system, in which I analyzed the phenomenon of non-radiative energy transfer, are spherical inorganic nanoparticles with organic fluorophores on the surface.

In the works discussed within the habilitation cycle, I presented the proposed by me model for a theoretical description of the Förster resonance energy transfer (FRET) phenomenon on spherical core-shell nanostructures (**paper H8**) and the experimental verification of its selected aspects (**paper H9**).

Nonradiative energy transfer on spherical nanostructures

The **paper H8** discusses a theoretical model describing the case of energy transfer in one step for a two-compound donor-acceptor system placed on a spherical nanostructure. Spherical nanostructures with various types of fluorophores attached resemble artificial nanoscale antenna systems and can also act as a broadband light sources. They also constitute a starting point for the research and design of multifunctional spherical core-shell systems, with different properties of both the core and the shell, for which the spectrum of applications is very wide [58, 59].

The model I propose in the **paper H8** describes the nonradiative energy transfer on a spherical nanoparticle, to the surface to which two types of fluorophores are attached: donors (D) and acceptors (A), which are much smaller in size than the nanoparticles. An example of such a system is a core-shell nanoparticle. We assume that there is no energy migration between donors and acceptors and no reverse energy transfer from acceptors to donors and that the fluorophores are randomly distributed on the surface of the nanoparticle. In such a system, an excited donor transfers the excitation energy to acceptor in one step. Furthermore, we assume that the concentration of nanoparticles is so low that the excitation transfer between different nanoparticles can be neglected.

The theoretical quantity that is of interests is the probability density $P(t)$, that a donor that was excited by a δ -pulse of light at time $t = 0$, will still remain in the excited state at some later time t . This quantity is the solution of a differential equation that takes into account the deactivation processes of the excited donor, such as photon emission and energy transfer to acceptors. Donor fluorescence decay is calculated by averaging the function $P(t)$ over the spatial distribution of acceptors, taking into account the rate constant of energy transfer from an excited donor D to the unexcited acceptor A . The resulting expression for the fluorescence intensity decay depends on the radius of the nanoparticle R and the number of acceptors N (**equation 17 at work H8**).

In most experimental studies, it is difficult to prepare spherical nanoparticles with virtually identical radii. Therefore, to make it possible to apply theoretical considerations to a wider range of experimental data, I have taken into account the probabilistic nature of nanoparticle sizes. The previously

obtained fluorescence decay of donors was additionally averaged, assuming a Gaussian distribution of nanoparticle radii with mean $\langle R \rangle$ variance σ (equation 21 in paper H8).

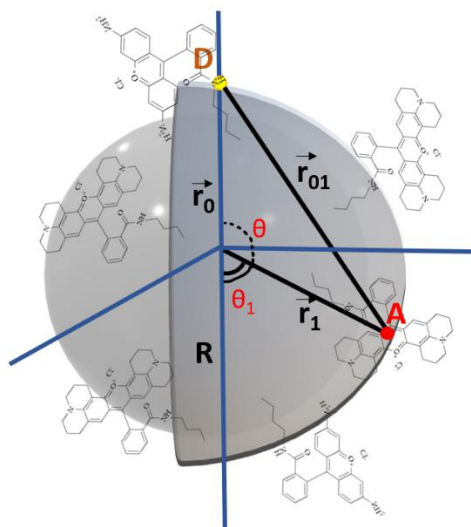


Figure 4. A schematic diagram of a core-shell nanostructure with distributed donor (D) and acceptor (A) molecules of the electronic excitation energy. The vectors \vec{r}_0 , \vec{r}_1 – denote the position of the donor and acceptor on the surface of the core-shell nanoparticle, respectively, the value of the vector \vec{r}_{01} – the distance between the donor and acceptor, while R – the radius of the nanostructure. The angle θ is the angle between the vectors \vec{r}_0 , and \vec{r}_1 and θ_1 – is the angle between the vector \vec{r}_1 and the vertical axis of the coordinate system.

The correctness of the model was verified by comparing the predicted results with the results of the Monte Carlo simulations, using the previously described step-by-step algorithm. In the simulation, one donor and N acceptors were placed uniformly on the surface of a sphere of radius R . Molecules on the surface of the nanoparticle are assumed to behave as point dipoles, and an averaged orientation factor of 0.476 was assumed in the Förster rate constant, which corresponds to a static dipole system. Monte Carlo simulations of fluorescence intensity decay were carried out for two example-nanostructures with an average radius of $\langle R \rangle = 25$ nm (smaller nanoparticles) and $\langle R \rangle = 50$ nm (larger nanoparticles). The value of the critical radius R_0^{DA} was 5 nm and corresponded to a real R110 (donor)-R101 (acceptor) system.

Figure 1 in paper H8 shows a comparison of theoretical results (described by **equation 17 in paper H8**) with results obtained using the Monte Carlo simulations of fluorescence intensity decay in donor-acceptor systems with different numbers of acceptors (from 5 to 500), distributed on core-shell nanostructures with two different radii: (a) $R=25$ nm and (b) $R=50$ nm. These results show excellent agreement between the theoretical calculations and the Monte Carlo simulation results for both small and large nanoparticles (in terms of the values of their average radii).

It is worth noting that for smaller nanoparticles with a radius of $R=25$ nm, even for a relatively small number of acceptors, the decay of fluorescence intensity occurs very quickly, which is due to the efficient energy transfer from the donor to closely located acceptors. For larger core-shell nanoparticles ($R=50$ nm), the fluorescence intensity decay curves differ slightly for a small and moderate number of acceptors, because the average distance between potentially interacting molecules is much larger in

this case. This leads to a weaker energy transfer between R110 and R101 compared to smaller nanoparticles with the same number of acceptors.

Analyzing the results shown in **Figures 1a and 1b (in paper H8)** and also performing a number of further detailed calculations not included in the cited paper, I could spot that the smaller the ratio of the nanoparticle radius (R) to the critical radius for excitation energy transfer R_0^{DA} , the faster the decay of the fluorescence intensity of the donor. This is related to the fact that the energy transfer to acceptors mainly occurs in the local vicinity of the excited donor molecule.

In laboratory conditions, it is difficult to obtain nanostructures with nearly identical radii, so a study was conducted to see if and to what extent the distribution of nanoparticle radii affects the energy transfer.

Figures 2a and 2b (in paper H8) show the results of the Monte Carlo simulations of donor fluorescence intensity decay in the presence of the excitation energy transfer between randomly distributed D and A molecules on the surface of core-shell nanoparticles. The donor fluorescence decay is presented as a function of the number of acceptors for selected values of the Gaussian distribution parameters of the core-shell nanoparticle radii: (a) mean value $\langle R \rangle = 25$ nm and variances $\sigma = 2.5$ nm and $\sigma = 5$ nm, respectively; (b) mean value $\langle R \rangle = 50$ nm and variances $\sigma = 5$ nm and $\sigma = 10$ nm, respectively (i.e. with a constant relative standard deviation σ of 10% and 20%). It follows from **Figure 2a** that the decay of donor fluorescence becomes slightly slower as the standard deviation of the Gauss distribution of nanoparticle radii increases in the Monte Carlo simulation, when compared to the results of the Monte Carlo simulations with a fixed nanoparticle radius R equal to the mean value of $\langle R \rangle$. This effect becomes more pronounced as the number of acceptors increases, and for $N > 100$ it cannot be neglected. While for larger nanoparticles with an average radius of $\langle R \rangle = 50$ nm with a standard deviation of 10% and even 20% (**Fig. 2b in paper H8**), this effect is negligible small, even for a large number of acceptors. **Figures 2a and 2b** also show how efficient tool are the Monte Carlo simulations in describing complicated systems. The results of the Monte Carlo simulations for larger nanoparticles with an equal radius of $R = 50$ nm differ little from those of the Monte Carlo simulations considering the Gaussian distribution of their radii with a mean value of $\langle R \rangle = 50$ nm with a standard deviation of 10% and 20%. This correspondence, however, decreases evidently while dealing with small nanoparticles with a large number of acceptors connected to them. From **Figure 3 (in paper H8)**, we found a strong nonlinear dependence of donor fluorescence decay on the core-shell radius quotient to the critical Förster radius R/R_0^{DA} , for particular time instants, for example $t/\tau_{0D} = 1$.

A comparison of the results of the Monte Carlo simulations and the general theoretical model (**Equation 21 in paper H8**) for selected numbers of acceptors and different parameters of the Gaussian distribution of core-shell nanoparticle radii with $R = 25$ nm and $R = 50$ nm is presented in **Figures 4a-d (paper H8)**. It can be clearly seen that the theoretical calculations based on Equation 21 correspond perfectly with the results of the Monte Carlo simulations, which is particularly evident even with large particle numbers and significant standard deviations. This confirms the correctness of the adopted theoretical model.

In addition, the paper compares the results of the Monte-Carlo simulation and theory (**equation 21 in paper H8**) for the average lifetimes values of donors randomly distributed on the surface of a sphere with 25 nm and 50 nm radii (**Fig. 5 in paper H8**). The results are presented as a function of the number

of acceptors for the selected Gaussian distribution parameters. Again, we observe a very good agreement between the simulation results and the theory. Similarly, as it took place in case of the fluorescence intensity decay of donors, also for the average donor lifetime values, taking into account the size distribution of the nanoparticle radii leads to an increase of the average donor lifetimes. This effect is, as expected, larger for small nanoparticles with radii $R=25$ nm radii (**Fig. 5a in paper H8**) where we observe an almost twofold increase in the relative average donor lifetimes. For large $R=50$ nm nanoparticles, the effect is more subtle, while in both cases it can be seen that for a fixed number of acceptors, the lifetime increases as the variance of the Gaussian distribution increases.

The creation of this type of theoretical model was intended not only to fill the gap in the theories describing nonradiative energy transfer, but also the possibility of its later applications to estimate, for example, the average number of fluorophores populating nanoparticles or to obtain information on the type of the size distribution of the synthesized nanoparticles (not necessarily always it is supposed to be a Gaussian distribution). An example of spherical nanostructures are core-shell nanostructures. These structures consist of at least two components, often chemically, physically or structurally different from each other. These components possess properties of the materials that make them up, as well as those that result from the interactions between them. The outer layer protects the core from physical or chemical factors, related to contact with the environment, and improves its stability or simply gives the material a new functionality (such as the ability to emit light) [33, 59, 60]. Besides, coating the core with relevant layers can improve reactivity, thermal and oxidative stability, protect against aggregation, and reduce the cytotoxicity of the synthesized systems. A properly selected shell also creates the possibility of further modification of nanostructures depending on the area of their planned applications, e.g. creating antenna-like systems. The process of a shell modification can take place by attaching to it chemical compounds by creating permanent covalent bonds or electrostatic interactions and Van der Waals forces (**paper H9**). Due to all these interesting properties of core-shell nanostructures, allowing future continuation of research with interesting multi-component systems, I chose them to verify the theoretical model of electronic excitation energy transfer on spherical nanostructures described in **paper H9**. The results were described in **paper H9** of the habilitation cycle. In cooperation with the Faculty of Chemistry of the University of Gdansk, a system was built that I designed, in which fluorophores of: rhodamine 110 as an excitation energy donor and rhodamine 101 as its acceptor, were connected to the specially modified for this purpose surface of $\text{TiO}_2@\text{SiO}_2$ nanostructures. The obtained nanocomposite is named in this work as $\text{TiO}_2@\text{SiO}_2\text{-(CH}_2\text{)}_3\text{-NH-D/A}$. As the efficiency of the energy transfer depends on, among other things, the number of fluorophores and the intermolecular distances, two types of samples were prepared, strongly differing in the ratio of the number of donors to the number of acceptors, so as to investigate the two interesting cases: typical energy transfer in one step or multi-step energy migration ending with energy transfer to acceptors. The variant in which the molecules were covalently bound to the $\text{TiO}_2@\text{SiO}_2$ nanoparticle in a ratio of 1 donor molecule to 350 acceptors was named D_{TRA} , while the structure with 350 donors per 1 acceptor was denoted D_{MIGA} .

After describing the synthesis and properties of the obtained nanostructures, the fluorescence intensity decays for these two antenna-like systems (D_{TRA} , D_{MIGA}) was presented in the paper and then their agreement was assessed with the theoretical model of a one-step energy transfer, including the nanoparticles size distribution, discussed in detail in **paper H9 (Fig. 5ab of paper H9)**. Furthermore, the consistency of the model was tested by the Monte-Carlo simulation method.

In case of the $D_{MIG}A$ system, we practically deal with emission by donors, so the decay observed in **Fig. 5a (in paper H19)** is almost monoexponential with a fluorescence decay time of 3.82 ns. The situation is different, however, for the D_{TRA} system. Here the decay is non-exponential and the decrease in donor fluorescence intensity is much faster than for the $D_{MIG}A$ system. This is due to the trapping of the excitation energy by closely located acceptors (without energy migration in the set of donors). Fig. 5b shows, in addition to the experimental results, also the data obtained based on a theoretical model (**equation 21 in paper H8**) and the results of the Monte-Carlo simulations carried out presuming the following energy transfer parameters: $R_0^{DA} = 5 \text{ nm}$, $\eta_{0D} = 0.98$, $\tau_{0D} = 3.82 \text{ ns}$, $\langle \kappa^2 \rangle = 0,476$. To verify the experimental data I used a model that takes into account the probabilistic nature of the distribution of nanostructure radii, applying the Gaussian distribution for the nanoparticle radii, because, as shown in **Fig. 1 (paper H9)**, in the tested system we are not dealing with identical nanoparticles but with a certain statistical distribution of their radii, which was examined on the basis of photos of nanoparticles obtained using transmission electron microscopy. As one can see, the distribution is almost symmetrical with a maximum for $R = 75 \text{ nm}$ and a half-width of 13 nm.

Both in case of the theoretical model and the Monte-Carlo simulations, under the assumption the radius of spherical nanoparticles equals $R = 75 \text{ nm}$, the best fit to the experimental results was obtained for the nanoparticle population in the ratio of 1 donor molecule to 335 acceptors.

This number turned out to be very close to the estimate of 1/350 obtained during the independent experimental procedure described in the paper [60].

Additionally, in my work I presented the results of the Monte-Carlo simulations of the average number of the excitation energy jumps in the set of donors, when we deal with strong energy migration (**Fig. 6 in paper H9**). It can be seen that under the experimental conditions ($\langle R \rangle = 75 \text{ nm}$) energy migration is a very intense process and the excitation energy can jump many times (the average number of jumps is about 1325). At the same time, **Fig. 7 (paper H9)** it is clear that despite the large number of jumps between donors, the excitation energy remains located relatively close to the place of initial excitation, which as evidenced by the value of the relative mean square shift of the excitation energy in the energy migration process for $N = 335$ donors. This is probably the result of strong excitation energy remigration on the spherical nanoparticle, indicating the non-Markovian character of this stochastic process.

To summarize, the scientific achievement presented in works H8 and H9 consists in the creation of a theoretical model describing the case of energy transfer in one step for a two-compound donor-acceptor system placed on a spherical nanoparticle, taking into account the distribution of the radii of these nanoparticles and experimental confirmation of the model effectiveness in the description of experimental results. Moreover, the Monte-Carlo simulations allowed to correctly describe the experimental results of the system in which the energy transfer is preceded by its multi-stage migration.

I currently work on an analytical model describing multi-stage energy migration followed by the non-radiative transfer of excitation energy, also on a spherical nanoparticle with chemically linked donors and acceptors. In order to obtain an approximate expression for the decay of the donor fluorescence intensity, I employed the three-body Padé approximation in a selfconsistent diagrammatic model. The

results of this model are currently under verification using the Monte-Carlo simulations and experimental data, on a representative donor-acceptor system placed on a spherical nanoparticle. The preliminary results are very promising for a small and moderate number of fluorophores on the nanoparticle surface ($N < 75$).

Orientalional factor and its effect on selected properties of nonradiative energy transfer

As a rule, it is assumed that nonradiative energy transfer can occur at distances of up to 10 nm between interacting molecules, with the transfer already generally very inefficient at such a large distance. In recent years, the need to increase the useful range of donor-acceptor energy transfer has been noted, not least because of the great importance of this process for conformational studies of biologically active macromolecules. Some qualitative success in this regard has been achieved using the phenomenon of light-induced interaction of the dipole moments of the transition of fluorophores with surface plasmons on metallic nanostructures. However, there are still many difficulties in a consistent analytical and numerical description of the mechanism of such energy transfer enhancement. In particular, the derivation of a universal expression for the rate constant on energy transfer as a function of the distance of interacting emitters in the presence of surface plasmons taking into account different geometrical configurations of interacting molecules is a very complicated task. Therefore, for the time being, the research in this stream is mainly qualitative and it is difficult to extend the scope of the "spectroscopic ruler" [20], which is often referred to as energy transfer at the nanoscale, with their help.

Thus, an important task remains to try to create an alternative potential method by which to try to increase the effective range of energy transfer. A satisfactory qualitative result was obtained by the authors in the work (Koushik, S. V.; Blank, P. S.; Vogel, S. S. PloS One 2009, 4 (11), e8031.) [61], where one acceptor was replaced by two or three molecules, thus obtaining an average increase in the range of energy transfer. In the **H2 publication**, we decided to design a model system, where ideally several closely located and non-aggregating acceptors are arranged on a polypeptide or protein, acting as an antenna system pulling excitation energy from a single donor. The distance between acceptors distributed on a single biomacromolecule is a small fraction of the average distance between the donor and the set of acceptors, so we are dealing with a donor group of closely located acceptors system.

Then the dynamics of such a system may be described by equations **1 and 2 (paper H2)**, in which the following processes are considered: nonradiative and radiative deactivation of the excited state of donor with the rate constant $1/\tau_{0D}$ and energy transfer from donor to acceptor with the rate constant w^{DA_i} .

The solution to this set of equations leads in a simple way to the relations for donor fluorescence intensity decay and its quantum yield in the presence of energy transfer to strong acceptor trap (**Eqs. 6 and 7 in paper H2**). Similarly to other previously described works the correctness of the obtained formulas has been verified by Monte-Carlo method.

The obtained effect is visible in **Fig.2 (paper H2)** which presents an example of the course of relative donor fluorescence quantum yield versus the distance between interacting donor and traps. Solid curves correspond to relative donor fluorescence quantum yield for random and static orientations of

acceptor transition moments. The set of solid curves indicates the possibility of distinct enhancement of effective range of energy transfer. For example for the system donor- trap (consisting of 10 acceptors) at mean distance of interacting molecules $R=11$ nm the efficiency of transfer is very high and it attains about $\frac{1}{2}$. Mention should be made that usually at such a large distance energy transfer to a single acceptor is negligible.

An attractive idea, though significantly more demanding in practice, is to study energy transfer efficiency from excited donor to the multiple acceptor trap but for parallel transition moment orientation of all acceptors (and that of the donor). This case is illustrated by the set of dotted curves in **Fig.2 (H2)**. In this case it was difficult to provide analytical solution but it was possible to perform Monte-Carlo simulations for several traps containing different numbers of acceptors.

In this case energy transfer from donor to trap consisting of 10 acceptors has efficiency equal to about $\frac{1}{2}$ at significantly larger distance $R=16$ nm. At a distance $R=20$ nm this efficiency drops to about 0.2 which seems to be a sensible upper distance limit to get reliable information.

I am aware that during designing and production of real antenna systems we have to deal with several problems like limited number of sites to which acceptors can be linked to the macromolecule, possible aggregation or some problems with accurate orientation of transition moments. However, immense progress in chemical and material technologies may make the idea realizable.

The idea itself has its roots in other studies I performed at first during my Ph.D. and next after completing Ph.D. These studies concerned energy migration in uniaxially oriented polymers (before Ph.D) and energy transfer in similar but two-component donor-acceptor systems.

My early studies in one component systems have shown that introducing high degree of order of transition moments directions leads to extreme changes in concentration courses of emission anisotropy compared to disordered systems. Further experimental studies in partly ordered two-component donor-acceptor systems (**paper H5**) have shown that even moderate but different ordering of transition moments of donors and acceptors transition moments directions leads to spectacular changes in the courses of emission anisotropy spectra.

Polymeric film is a medium in which we can quite easily control the degree of order of transition moments of molecules participating in energy transfer. Therefore, the served in **paper H5** to analyse the effect of mutual orientation of transition moment directions of donor and acceptor on the properties of energy transfer.

During the uniaxial stretching of polymer film transition moments of linear elongated molecules show strong tendency to orientate towards this direction.

To describe the angular distribution of directions long axes of linear molecules at a given stretching degree Tanizaki function has been applied [62]:

$$f_g(\mathcal{G}_i) = R_S^2 \sin \mathcal{G}_i \left\{ 1 + (R_S^2 - 1) \sin^2 \mathcal{G}_i \right\}^{\frac{3}{2}} \quad (35)$$

where: ϑ_j – angle formed by long axis of j-th molecule with the orientation direction of polymer matrix and R_S – denotes the degree of stretching of the film.

In all theories of excitation energy transport in disordered systems the assumption is made that the contribution to the observed emission anisotropy is given only by molecules initially excited by the linearly polarized light beam. The geometrical change of the system induced by stretching leads to the situation that this assumption is no longer fulfilled. **In paper H5** experimental data and Monte-Carlo simulations of emission anisotropy in three different donor-acceptor systems are provided.

Each of them behaved differently in view of specific orientation of transition moments of donor and acceptor.

For the system of elongated linear fluorophores DOCI (donor) and DTCl (acceptor) transition moments of both molecules are located along the long molecular axis (confirmed by linear dichroism studies) and they oriented towards the axis of polymer stretching. DOCI (donor) R101 (acceptor) system was in turn characterized by high degree of orientation of donor transition moment and low orientation of acceptor transition moment (as rhodamine 101 is not an elongated molecule). In the case of acridon (donor) – DOCI (Acceptor) system the transition moment of donor is located perpendicular to its longer molecular axis.

As shown in **paper H5**:

- For elongated molecules (DOCI,DTCl) the preferential distribution of transition moments directions of donors and acceptors relative to the direction of film stretching leads to the preservation of emission anisotropy in the acceptor band despite energy transfer from donor to acceptor (Fig.1a in work H5). In disordered polymer film classical depolarization effect of acceptor fluorescence is visible.
- For DOCI-R101 system (**Fig.1b in paper H5**) strong depolarization in acceptor fluorescence band is observed as a result of energy transfer from donors moments oriented preferably towards the direction of film stretching to acceptors which remain almost randomly oriented even after film stretching. Consequently, increase in stretching degree leads to much more pronounced increase of donor anisotropy than that of acceptor.
- In the case of the third system acridon-DOCI (**Fig.1c, paper H5**) after excitation in the donor band and observation in the acceptor band for disordered system almost complete depolarization of fluorescence is observed as a result of energy transfer from donors to randomly distributed acceptors.

However, with the film stretching we can see nontypical behavior of anisotropy in the donor fluorescence band. Emission anisotropy decreases in this band with the increasing stretching of the film, which is due to the tendency of transition moment of donor to orientate perpendicularly to the axis of stretching. Simultaneously we can observe significant repolarization effect in the acceptor fluorescence band. Additionally, emission anisotropy of DOCI (acceptor) even in the strongly stretched system ($R_S=5$) does not attain in the acceptor fluorescence band so high values as in formerly discussed systems. The reason is the contribution of relatively weakly polarized donor fluorescence to the total fluorescence observed at longer wavelengths (acceptor fluorescence band).

Based on the described emission anisotropy courses we can conclude about evident role of orientational factor (mutual orientation of transition moments of donors and acceptors) in preservation or loss of emission anisotropy after the energy transfer.

Table 1 (paper H5) shows how pronounced are the changes in the averaged orientation factor induced by stretching the films and ordering of transition moments.

Contrary to one component systems, where we deal with a single value of averaged orientation factor, in two component partly ordered system more than one orientation factor must be introduced. They can have quite different values for donor-donor interactions and donor-acceptor interactions depending on the orientation directions of transition moments of interacting species. As can be seen the averaged values of orientational factor in uniaxially oriented matrix can differ strongly from well-known values commonly assumed in disordered systems (0.476 the case of static and 2/3 the case of dynamic randomly distributed dipoles). For example, for the first system DOCI-DTCl, for strongly stretched film ($R_s=5$) the value for energy transfer $\langle \kappa_{DA}^2 \rangle = 1.25$ is much bigger, however, for third discussed stretched system (acridon-DOCI, $R_s=5$) the averaged orientational factor for energy transfer is much smaller $\langle \kappa_{DA}^2 \rangle = 0.43$ which obviously leads to respective increase or decrease of critical radius for energy transfer. The values of averaged orientational factors have been obtained from Monte Carlo simulations according to the procedure described. The same table contains the averaged values of orientation factors calculated for donor-donor and acceptor-acceptor interactions evidencing its strong dependence on the mutual orientations of interacting species.

The results of emission anisotropy intensity decays shown for donor and acceptor of excitation energy (**Figs. 2 and 3 in paper H5**) are in agreement with those of steady-state emission anisotropy and indicate qualitatively similar in character differences for ordered and disordered systems. They can be shortly summarized as follows:

- for disordered (DOCI-DTCl) system donor emission anisotropy decays much faster than in the case of ordered systems (**Fig.2, paper H5**). In the ordered system acceptor emission anisotropy does not decrease over the whole time window. This is again the result of strongly correlated directions of transition dipole moments of donors and acceptors. The initial polarization of excited molecules is preserved in the system over the time of experiment;
- the effect of energy transfer from donor to acceptor in the system acridon-DOCI (**Fig.3 in paper H5**) is quite different as it occurs between the populations of molecules with completely different orientations of transition moments of donors and acceptors. Fluorescence anisotropy decay in the donor fluorescence band in the ordered system is quite nontypical as its course starts from lower initial values compared to the anisotropy decay in the acceptor fluorescence band. This corresponds again to steady-state anisotropy spectra in Fig. 1c.

The achievement presented in the two above works consists of showing that in systems with partial organization of fluorophore transition moments, there exist significant reserves related to the control of the efficiency and directionality of the energy transfer by analyzing the value of the orientation factor. I proposed a method of increasing the effective range of energy transfer in macromolecules by connecting linking several closely located identical acceptors with the same orientation of transition moments. The Monte-Carlo simulation studies showed that the effective range of the energy transfer could be increased 2-3 times, even to a dozen or so nanometers. On the other hand, in

polymer systems with partial ordering of the transition moments of donors and acceptors, it is possible to control the degree of anisotropy of the acceptor emission (i.e. a certain type of optical information) after energy transfer, by changing the value of the orientation factor. Two elements are decisive here: the mutual location of the appropriate directions of the donor and acceptor transition moments and the degree of order of the system. Appropriate choice of the donor and acceptor molecules and of the changes in the polymer stretching factor can, in principle, allow to obtain a very diverse and well-controlled emission anisotropy after energy transfer. This may be useful in the design of optical materials with polarization tuning.

Energy transfer as a tool for detecting and testing MMP-9 metalloproteinase activity.

The Förster model of energy transfer can be used to determine intra-molecular distances and determine the conformation of macromolecules in biological systems. This method used classically, is effective at distances not exceeding several nanometers, which is associated with the effective range of non-radiative energy transfer in typical donor-acceptor systems.

In the **publication H6** I examined the photophysical properties of peptide labeled at its ends with a donor and acceptor of energy, which serves as part of a biosensor allowing the detection and assessment of the activity of the enzyme matrix metalloproteinase 9 (MMP-9). MMP-9 appears in excessive concentration in the human body in the course of various diseases, including oncological basis. Therefore, the detection and determination of the concentration of this enzyme is important because it facilitates making an appropriate diagnosis [63, 64]. An attempt to respond to the indicated need is to develop the idea of a sensitive detection method based on the preparation of a dedicated peptide that is cleaved exclusively by the MMP-9 metalloproteinase. The figure below shows this peptide, which consists of appropriately selected molecules acting as a donor (7-amino-4-methyl-3-coumarinylacetic acid, AMCA) and an acceptor (5-carboxytetramethylrhodamine, TAMRA) of electronic excitation energy and a peptide chain connecting them (hereinafter I use the designation AMCA-PEP-TAMRA). In the absence of MMP-9 metalloproteinase, efficient energy transfer from the excited donor to the unexcited acceptor is observed upon donor excitation. The presence of metalloproteinase causes it to cut the peptide chain and, consequently, separate the donor and acceptor over much longer distances on average, preventing energy transfer from occurring.

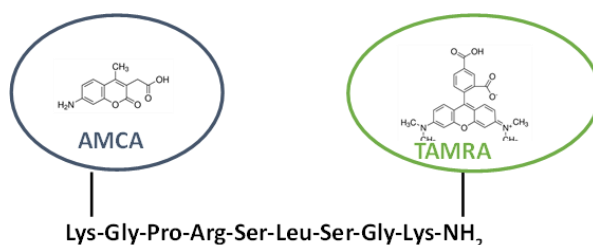


Figure 5. Schematic of the tested system AMCA-PEP-TAMRA (D-PEP-A).

The publication **H6** describes the selected spectroscopic properties of this peptide in glycerol. The most important part of this work is the analysis of the nonradiative energy transfer from the AMCA fluorophore to the TAMRA fluorophore to assess the conformational distribution of this peptide. This is very important to verify its suitability for testing the activity of the MMP-9 enzyme.

The maximum distance between the donor and the acceptor that can be attributed to the linear conformation of this peptide is 4.6 nm and is larger than the value of the critical radius for nonradiative excitation energy transfer in this system $R_{0DA} = 3.9$ nm, which I determined based on equation (2) based on spectroscopic measurements (AMCA and TAMRA absorption and fluorescence spectra and average donor fluorescence lifetime).

Fluorescence spectra measurements for the peptide with the donor, the peptide with the acceptor, and the AMCA-PEP-TAMRA system in dehydrated glycerol are presented in Figure 2 (**paper H6**). They indicate efficient transfer between the donor and acceptor connected to the peptide, through an obvious decrease in the fluorescence intensity of the donor accompanied by an increase in the intensity in the acceptor band.

This is also confirmed by emission anisotropy studies (**Figure 3 in paper H6**) where, with the shift of the observation wavelength from the donor to the acceptor band, we observe a strong depolarization of the acceptor fluorescence when the donor is excited. In disordered systems, only molecules initially excited by light absorption contribute to the anisotropy of the observed fluorescence, in this case, the AMCA donor molecule. TAMRA molecules are excited mainly as a result of energy transfer from AMCA, therefore they emit highly depolarized light. Also, the results of fluorescence intensity decays (**Figure 4abc in paper H6**) leave no doubt that efficient energy transfer takes place between the molecules connected to the peptide because we observe:

- shortening of the donor's lifetime in the presence of the acceptor on the AMCA-PEP-TAMRA peptide (from 3.95 ns to 1.35 ns) and non-exponential decay of the donor's fluorescence intensity,
- in the range of short times after excitation, the acceptor fluorescence intensity curve increases (Figure 4c in work H6), which suggests the so-called "pumping" of the excited state of the acceptor as a result of energy transfer from the donor.

The efficiency of the electronic excitation energy transfer process can be easily determined from the following correlations:

$$E = 1 - \frac{f_{AD}}{f_D} \quad (36)$$

where f_D, f_{AD} – the fluorescence intensity of the donor linked to the peptide in the absence of acceptor and the donor fluorescence intensity in the presence of acceptor which partly quenches donor fluorescence, respectively, and

$$E = \frac{R_{0DA}^6}{R_{0DA}^6 + R^6} \quad (37)$$

R_{0DA} – the critical distance for donor to acceptor energy transfer, R -single donor-acceptor distance.

If we assume that the peptide is rigid and has a linear single conformation, then the donor and acceptor would be at the maximum possible distance from each other on the peptide. However, the efficiency of the energy transfer process calculated by me based on both compounds was dramatically different and amounted to $E=78\%$ (formula 36) and $E=26\%$ (formula 37), respectively. The reason for such a large discrepancy is the fact that the peptide connecting AMCA and TAMRA is flexible and shows a certain

donor-acceptor distance distribution, as a result of which their average distance is much smaller than the maximum distance ($R = 4.6$ nm). A correct description of energy transfer in such a system requires postulating a donor-acceptor distance distribution function and obtaining a correct description of the non-exponential decay of the donor fluorescence intensity.

For reasons of simplicity, I proposed a function of the Gaussian distribution of the distance between the donor and the acceptor on the tested peptide in the fluorescence decay law. In this case, it was shown in **paper H6** that the expected function describing the decay of the donor fluorescence intensity for the AMCA-PEP-TAMRA system is given by (**paper H6, formula 6**):

$$G(t) = \frac{B}{\sqrt{2\pi}\sigma} \int_0^{\infty} \exp\left(-\frac{R - \langle R \rangle}{2\sigma^2}\right) \exp\left(-\frac{t}{\tau_0} - \frac{t}{\tau_0} \left(\frac{R_{0DA}}{R}\right)^6\right) dR \quad (38)$$

where σ is the standard deviation of the unmodified Gauss function. It is noteworthy that σ is in a straight way correlated with the half-width δ of this distribution function by the relation:

The δ value provides important information about the conformation and the flexibility of the peptide upon the given experimental conditions. **Equation 6 (paper H6)** was used to describe the experimental data, which are well described by it in **Figure 4b (paper H6)** for $\delta = 2.79$ nm. The obtained value of the half-width of this distribution is rather high, indicating considerable conformational freedom of the peptide under study. In the detailed analysis, it was taken into account that the Gaussian distribution function should be "truncated" for small and large argument values due to the physical limitations imposed on the allowed distances of the donor and acceptor.

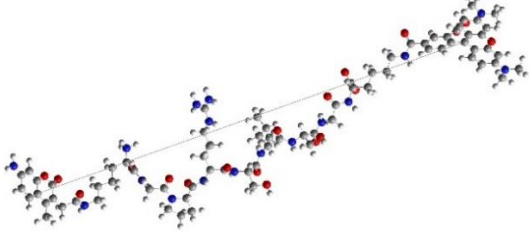
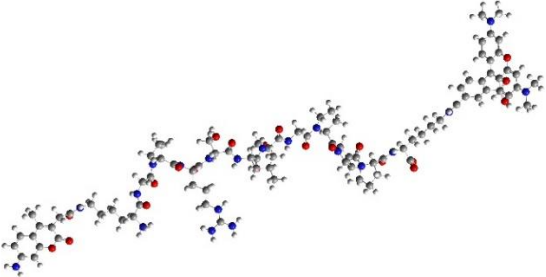
In summary, the experimental studies and their analysis carried out in the H6 paper confirmed that upon excitation of the donor in the AMCA-PEP-TAMRA system, efficient transfer of the excitation electronic energy occurs. In addition, I also showed that the use of a Gaussian distribution function to model the distribution of distances between the donor and acceptor of a connected flexible peptide in the equation describing the decay of fluorescence intensity yields results consistent with experience and the peptide itself shows high conformational freedom.

The next step was to test the usefulness of the invited AMCA-PEP-TAMRA system for studying the activity and concentration of the MMP-9 enzyme. In particular, the work consisted of studying the kinetics of the enzymatic reaction, that is, cutting the peptide connecting the donor to the acceptor with the MMP-9 enzyme (**paper H7**). The rate constant of the enzymatic reaction significantly increased as a function of MMP-9 enzyme concentration, causing strong changes in fluorescence spectra. These changes consisted of an increase in the fluorescence intensity of the donor as the enzyme's peptide-cutting reaction progressed. The direction of these changes was due to the changing spatial separation of the donor and acceptor as a result of peptide bond hydrolysis, leading to a decrease in the efficiency of energy transfer from the donor to the acceptor.

In this work, in addition to the AMCA-PEP-TAMRA peptide system characterized in paper H6, we also investigated its analog in the form of AMCA-PEP-3PRO-TAMRA elongated by the addition of three proline groups during synthesis (denoted as Pro - system 2 in the figure below). The goal was to increase

the freedom of access of the MMP-9 enzyme to the peptide chain and consequently increase the rate constant of the enzymatic reaction.

Table 1. AMCA-PEP-TAMRA and AMCA-PEP-3PRO-TAMRA systems used to examine the activity of the MMP-9 enzyme.

System 1	D-PEP-A	
System 2	D-PEP-3PRO-A	

Indeed, it can be seen in **Figure 2** and **from Table 2** in **paper H7** that the D-PEP-3Pro-A system is more efficiently cut by the metalloproteinase MMP-9. Table 2 in paper H7 contains detailed kinetic parameters of enzymatic hydrolysis for both systems, among others, the half-reaction time, that is, the time after which half of the amount of substance present at a given time will have reacted:

$$\tau_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{0,693}{k} \quad (39)$$

where k – the first-order reaction rate constant.

Its value decreases as the concentration of enzyme added to the system increases. It can also be seen that for the system with the longer chain, the half-life is shorter at 11 minutes compared to that for the D-PEP-A system, where its value is 23 minutes (at an MMP-9 concentration of $c=133\text{ng/ml}$). The observed linear dependence of the reaction rate constant k on the enzyme concentration c for both D- PEP-A and D-PEP-Pro-A systems presented in **Figure 3 in paper H7** allows them to be used to determine the amount of MMP-9 enzyme in a given system (**paper H7**). As it seems, the minimum sensible concentration of MMP-9 metalloproteinase that can be detected from a practical point of view, i.e., half-life, is 16 ng/ml for the shorter peptide system. The sensitivity of the longer peptide system for the presence of MMP-9 appeared to be even slightly higher.

The achievement in works H6 and H7 is showing the applicability of nonradiative energy transfer to evaluate the conformational properties of AMCA-PEP-TAMRA peptide a part of a biosensor to detect

metalloproteinase MMP-9. Making use of the Gauss distribution function to model the distance distribution between donor and acceptor on a flexible peptide in a relation describing donor intensity decay leads to a good description of experimental data and it proves high conformational mobility of the synthesized peptide. AMCA-PEP-TAMRA system and its longer analogue **AMCA-PEP-3PRO-TAMRA occurred to be sensitive indicators of the presence of metalloproteinase MMP-9 and they may be used to estimate the concentration of this enzyme in further studies .**

Summary

In the described cycle I have shown that the description of energy transport phenomena and its trapping in diversified systems may be described successfully by the set of analytical models in Monte-Carlo simulations as a main tool in systems of higher degree of complexity for which the construction of analytical models leading to expressions for luminescence characteristics is either very difficult or even impossible. The presented set of undertaken and described problems should not be treated as a closed, completed catalogue. In contradiction I did my best to show that both in the undertaken issues and related problems huge scientific resources and needs remain . An example of such unrealized need is for example derivation of a universal expression (for a variety of geometries) for the rate constant for energy transfer in the presence of surface plasmons. This would enable biological to extend the useful range of energy transfer as a spectroscopic ruler distinctly beyond 10 nm. This is in turn very important to study in more detail bigger macromolecules , designing novel biosensors and optical nanomaterials. Simultaneously, I consider very important to elaborate model of energy transfer suitable for other nanostructures , for example containing magnetic core. I would like to focus on these and some other problems I participated in beside my habilitation tasks will be my main points of interests.

For most important achievements presented in the habilitation cycle H1-H9 I consider:

- Analysis of the nonradiative electron excitation energy transfer in thin-film porous matrices, demonstrating that it is crucial and necessary for a correct analysis to take into account the non-uniform distribution of fluorophores in the matrices, and developing a method for determining the local concentrations of fluorophores in such hybrid materials. The method is based on the comparison of experimental results of fluorescence intensity decays with the results of the Monte Carlo simulations of the excitation energy transfer processes. Analytical approaches previously developed for disordered systems with a statistical distribution of fluorophores cannot be directly applied here.
- Development of the energy transfer model for the donor-acceptor system on spherical nanoparticles, taking into account the radius distribution of the nanostructures, obtaining within this model expressions describing fluorescence intensity decays for nanostructures of a specific radius as well as for the Gaussian radii distribution, and, finally, experimental verification of the data resulting from this approach.
- Employment of the nonradiative energy transfer to assess the conformational properties of a specially designed peptide as part of a biosensor for detecting the MMP-9 metalloproteinase. The analysis revealed significant conformational freedom of this peptide, manifesting itself with a relatively high half-width of the donor-acceptor distances distribution. The considered peptide as

well as its analogue appeared to be sensitive indicators of the MMP-9 metalloproteinase presence and can potentially be used to estimate concentration of this enzyme.

- I showed on two examples that in partially organized systems there exist significant reserves related to controlling the efficiency and directionality of energy transfer by analyzing the values of the orientation factor. I proposed an idea to extend the range of the energy transfer as a spectroscopic ruler based on linking several acceptors with the same orientation moments on the macromolecule. The Monte-Carlo simulations showed that the effective range of energy transfer due to the interaction of a donor with a set of such acceptor antennas could be increased to a dozen or so nanometers. On the other hand, in polymer systems with partial ordering of the transition moments of donors and acceptors, the degree of anisotropy of the acceptor emission (optical information) after energy transfer can be controlled by changing the value of the orientation factor. Two things are decisive here: the mutual orientation of the appropriate directions of the donor and acceptor transition moments and the degree of order of the system. Appropriate choice of donor and acceptor molecules together with the above-mentioned parameters allows to control the level of acceptors emission anisotropy to large extent.

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5. Presentation of significant scientific or artistic activity carried out at more than one university, scientific or cultural institution, especially at foreign institutions.

In 2008, I won a prestigious international competition for a research Maria Skłodowska-Curie scholarship under the 7th EU Framework Program and spent 1.5 years in a world-class laboratory of Prof. A. Douhal in Toledo. During this internship, I became familiar with, among others, modern experimental methods of femtosecond fluorescence spectroscopy, while being involved in research on the interactions of porphyrins with selected proteins (e.g. human serum albumin) or zeolite-like nanomaterials. Such studies make it possible to track the intermolecular interactions of the mentioned objects in the shortest time gaps currently reachable after the excitation of the system (starting from about 20 femtoseconds) and are vital, for example, for explaining molecular mechanisms important in transport phenomena of biologically active substances to organisms. Within this project, two papers were published [3 and 4 in attachment 4B (list of all publications after obtaining the PhD degree)], of which I am the first author.

6. Presentation of teaching and organizational achievements as well as achievements in popularization of science or art

Teaching achievements

I started my employment at the Institute of Experimental Physics, Faculty of Mathematics, Physics and Informatics, University of Gdansk, at a research-teaching position, therefore, since the very beginning I have had a range of teaching duties. These are classes covering a wide range of topics: from the so-called fundamentals of physics (mechanics, electromagnetism, thermodynamics) to specialized subjects (luminescence, molecular spectroscopy including biological systems, didactics of physics, mechanoscopy, environmental physics). And they have a variety of forms, as there are laboratory classes (9 different), auditory exercises (12 different), lectures (3 topics). To date, 6 students have written and defended bachelor's theses and 8 students master's theses. I have also been an assistant supervisor of 3 doctoral students; all the dissertations have been recognized outstanding. Currently, I am an assistant supervisor of still another doctoral student. Besides, I am also a subject matter and methodological supervisor for students practicing teaching of physics in primary and secondary schools.

All the classes that I taught had an original, authorial character, I created my own teaching materials for students: course books, sets of tasks and exercises, guides for the exercises carried out by students in a specialized didactic physics laboratory. The teaching materials that I made supported not only the classes I taught myself, but were meant also as an extension of the educational offer of the Faculty of Mathematics, Physics and Informatics aimed at the students of my home faculty, as well as other faculties of the University of Gdansk.

In an effort to improve the quality of education of students at my home faculty, I engaged myself in projects financed, for example, by European Union funds. I can state here my participation in the Operational Program "*Program for implementing modern elements of education at the University of Gdansk*" and within this project I created a set of instructions for laboratory exercises for students at the Laboratory of the Didactics of Physics (Physics Laboratory II). Involvement in another project "*We*

educate professionals – a comprehensive education program addressed to students, graduates and disabled students of the University of Gdansk resulted in co-authorship of the course books "*Fundamentals of physics I, II, III for medical physics students – exercises and tasks*" (this course book covered aspects of material point and rigid body mechanics, thermodynamics and electromagnetism) and also "*Fundamentals of modern physics for medical physics students exercises and tasks*". Still another project in which I participated was a project under the Human Capital Operational Program "*University of Tomorrow: Internationalization of education at the University of Gdansk through collaboration with the University of Houston-Downtown*"; within this project I wrote a course book "*Microscopy applications in biotechnology*" for biotechnology students.

With regard to activities to improve the quality of education at the University of Gdansk, I can recognize as my major contribution the development of didactic cooperation between the Institute of Experimental Physics of the Faculty of Mathematics, Physics and Informatics and the Faculty of Law and Administration of the University of Gdansk. In 2016, I prepared conceptually, substantively and didactically set of laboratory exercises for the *Criminology* field of studies, *Criminalistics* specialty, of the general academic full-time and part-time studies realized at the above-mentioned Faculty of Law and Administration. Introduction of these classes into the *Criminology* studies program enabled the students to gain practical knowledge of modern methods and techniques used in forensic sciences, originating in physics. Thanks to my efforts, the Physical Forensics Laboratory is constantly being improved and developed and to financially support these activities I managed to obtain two grants from the Teaching Initiatives Fund of the University of Gdansk; I was also the PI of both projects.

While trying to improve the quality of education at the University of Gdansk, I remember also about development of my own professional competences. I participate in a variety of training courses aimed at expanding both my knowledge of the subject matter of my teaching field, research topics, and teaching methods of conducting classes (e.g., tutoring).

I also provided consultation and proofreading of experimental chapters of the book by renowned scientists: Z. Gryczynski and I. Gryczynski "*Practical Fluorescence Spectroscopy*", CRC Press, Taylor&Francis Group, published in 2020, for which the authors honored me in the Introduction.

In 2019, in recognition of my teaching and educational achievements, I was awarded a Medal of the Commission of National Education. In 2023, I received a second rank Award of the Rector of the University of Gdansk for the entirety of my teaching and scientific achievements.

Achievements in the field of popularization of science

An important part of my activity as a physicist is the popularization of physics. Every year, I give several dozen hours of lectures and exercises at various levels, to primary and secondary school pupils. Since 2010 I have conducted about 300 hours of such classes. My classes appeared so popular that I was invited by the Pavel Adamowicz University High School in Gdansk to cooperation as a physics teacher.

My contribution to the popularization of science also includes my annual participation in the events such as the Baltic Science Festival, the Open Day of the Faculty of Mathematics, Physics and Informatics of the University of Gdansk, the Open Day of the University of Gdansk, the Educational Fair.

Another form of popularizing physics is my participation in projects aimed at creating opportunities for physics teachers to improve their professional qualifications. An example here can be my participation (as an expert in the physics group) in the project *Pomeranian (Voivodeship) – a good course for education. Supporting pupils with special predispositions in the field of mathematics, physics and computer science* under the Priority IX of the Human Capital Operational Program 2007–2013. And the outcome of this project were 8 extracurricular activities programs were developed, programs of academic meetings, science camps for pupils and workshops for teachers.

Organizational activities

- In 2013, 2015, 2017 and 2022 I was a member of the organizing committee of the international conference *International Workshop on Advanced Spectroscopy and Optical Materials*, the originator and main organizer of which was Prof. M. Grinberg (the idea of the conference is currently continued by Prof. Sebastian Mahlik from the Department of Condensed Phase Spectroscopy); I served as a secretary and co-secretary of the conference.
- In the years 2013 - 2023 I was a reviewer of many bachelor's and master's theses by students of the Faculty of Mathematics, Physics and Informatics and the Faculty of Chemistry of the University of Gdansk, and a member of the committees for diploma exams (both bachelor's and master's).
- In the years 2012 - 2019 I was, and since 2021 I am again, a member of the Council of the Faculty of Mathematics, Physics and Informatics of the University of Gdansk and the Council of the Institute of Experimental Physics, as a representative of assistant professor.
- In the academic year 2019/2020 I was a member of the Dean's Council.
- In the period 2014 - 2020, I was a member of the Team for tracking further activities and paths of university graduates. During my membership, I participated, as a member of the organizing committee, in the preparation of the Alumni Meeting of the Faculty of Mathematics, Physics and Informatics of the University of Gdansk (June 27, 2015).
- Since 2020, I have been a member of the Faculty's Team for updating the educational offer.
- In 2016 and 2017, I was an observer on behalf of the University of Gdansk during the A-level examinations in physics.
- I was a tutor of first-year students of Medical Physics (2011, 2018, 2019).
- I am a contributor to establishing and developing cooperation of the Faculty of Mathematics, Physics and Computer Science in the field of teaching with: the Faculty of Law and Administration and the Faculty of Chemistry of the University of Gdansk as well as with the Medical University of Gdansk.

List of conducted academic and science popularization activities:

Lectures given:

- *Biomolecules - Microscopy - application in biotechnology*; Biotechnology, full-time undergraduate studies
- *Mechanoscopy and physical methods of trace examination*; Criminology, full-time and part-time graduate studies

- *Microscopic techniques - Physics*; Medical Physics, full time graduate studies

Titles of the conducted auditorium exercises:

- *Physics*; Geology, full time undergraduate studies
- *Fundamentals of physics (mechanics and thermodynamics)*; Medical Physics, full time undergraduate studies
- *Mechanics of point particle, rigid body and particle*; Nuclear Safety and Radiological Protection, full time undergraduate studies
- *Elective lecture exercises: From molecular luminescence to nanocrystals and optical biomaterials*; Medical Physics, full time graduate studies
- *Elective lecture exercises: Principles of molecular spectroscopy*; Physics, full time graduate studies
- *Monograph lecture exercises: Selected topics of modern physics applications in medicine*; Medical Physics, full time graduate studies
- *Monograph lecture exercises: Optical biospectroscopy*; Physics, full time undergraduate studies
- *Monograph lecture exercises: spectroscopy of biological systems*; Medical Physics, full time undergraduate studies
- *Monograph lecture exercises: Selected physicochemical phenomena and characterization methods of biomaterials and biosensors*; Medical Physics, full time graduate studies
- *Monograph lecture exercises: Atomic and molecular spectroscopy*; Physics, full time graduate studies
- *Monograph lecture exercises: Principles of molecular spectroscopy*; Medical Physics, full time graduate studies
- *Lecture exercises: Microscopic techniques*; Physics, Medical Physics, full time graduate studies

Titles of conducted laboratory exercises

- *Information technology*; Sociology, Logopedics, Nature, Philology (Scandinavian studies), full time undergraduate studies
- *Physical laboratory 1*; Oceanography, Medical Physics/Fizyka, Physics (mechanics, Thermodynamics, electromagnetism, optics, spectroscopy), full time undergraduate studies
- *Specialist laboratory*; Medical Physics, full time graduate studies
- *Physical laboratory 2 (quantum physics and biophysics)*; Physics, full time undergraduate and graduate studies
- *Lecture exercises: Mechanoscopy and physical methods of trace examination*; Criminology, full-time undergraduate studies
- *Lecture exercises: Scientific techniques of examining traces of crimes using physical methods*; Criminology, full time undergraduate studies
- *Physics teaching practice*; Physics and Medical Physics, full time graduate studies
- *Master's degree laboratory*; Medical Physics, full time graduate studies
- *Environmental chemistry and physics - laboratory*; Environmental Health, Gdansk Medical University, full time undergraduate studies

List of scientific and popular science lectures and laboratory exercises conducted within a framework of partner scientific meetings and teaching events popularizing science:

- *Molecular spectroscopy and its role in biotechnology and medicine*; classes for high school pupils, Meetings with Physics, Faculty of Mathematics, Physics and Informatics, University of Gdansk, Lecture - 08.01.2015, laboratory exercises - 15.01.2015
- *Electrostatics and current*; classes for children from the „Bez rutyny” association, Faculty of Mathematics, Physics and Informatics, University of Gdansk, lecture - 18.04.2015
- *Luminescence around us*; classes for high school pupils, Meetings with Physics, Faculty of Mathematics, Physics and Informatics, University of Gdansk, Lecture - 03.12.2015, laboratory exercises - 10.12.2015
- *What is luminescence?*; classes for the Józef Wybicki Junior High School no 1 in Lębork, lecture - 05.12.2015
- *Luminescence around us – can drinking tonic shine?*; classes for high school pupils of the Państwowe Szkoły Budownictwa, Grunwaldzka 238, Gdańsk, „Pi” number day, invited lecture - 04.03.2016
- *Scanning electron microscopy and fluorescence phenomena*; youth classes related to the final of „Pomeranian Mathematical Matches”, Faculty of Mathematics, Physics and Informatics, University of Gdansk, demonstrations - 28.04.2016
- *Molecular spectroscopy and its role in biotechnology and medicine*; classes within the “Periodic Scientific Seminars of the Pharm-Phys-Chem Group”, Faculty of Mathematics, Physics and Informatics, University of Gdansk, invited lecture - 12.02.2016
- *World in a nanoscale seen through a microscope*; youth classes, Meetings with Physics, Faculty of Mathematics, Physics and Informatics, University of Gdansk, lecture - 27.04.2017
- *Fluorescence and methods of its enhancement and Applications of electron microscopy*; classes within the project „New Competencies - New Perspectives” for the 1st and 2nd class pupils of the Gen. Stefan Rowecki „Grot” School Complex no 1 in Zambrów, Faculty of Mathematics, Physics and Informatics, University of Gdansk, laboratory exercises - 13.06.2017
- *Can drinking tonic and candies shine?*; lecture for Everyone at the Experiment Science Center, Gdynia, Night of Scientists, invited lecture -3h - 29.09.2017
- *Fluorescence microscopy*; classes for the pupils of the Jan Paweł II High School no 5 in Torun, Faculty of Mathematics, Physics and Informatics, University of Gdansk, lecture - 26.10.2017
- *Fluorescence microscopy*; classes the pupils from schools of the Sztum district, Faculty of Mathematics, Physics and Informatics, University of Gdansk, laboratory exercises - 24.11.2017
- *Fluorescence microscope, Fluorescence phenomenon and methods of its enhancement*; classes for the pupils from the Wojsko Polskie Primary School no 39 in Gdansk, Faculty of Mathematics, Physics and Informatics, University of Gdansk, lectures - 07.12.2017, 08.12.2017
- *Microscope for the Nobel Prize*; classes for the pupils from the School Complex in Tujsk, Faculty of Mathematics, Physics and Informatics, University of Gdansk, laboratory exercises with elements of lecture - 08.02.2019
- *Principles of optical microscopy*; Cathedral and Division of Applied Pharmacy, Medical University of Gdansk, invited lecture - 27.03.2019
- *Miroscopy*; classes for junior high school pupils, „Talented from Pomerania”, Faculty of Mathematics, Physics and Informatics, University of Gdansk, lectures and laboratory exercises - 25.05.2019

- *Optical and electron microscopy and UV-Vis spectroscopy in a forensic laboratory – application examples*; Faculty of Mathematics, Physics and Informatics, University of Gdansk, lecture - 09-13.09.2019
- *Application of microscopy in forensic science, Observation of luminescence of organic compounds*; „Talented from Pomerania”, Faculty of Mathematics, Physics and Informatics, University of Gdansk, lecture exercises and workshop - 10-11.09.2019
- *Forensic traces and their disclosure*; „Talented from Pomerania”, Faculty of Mathematics, Physics and Informatics, University of Gdansk, forensic exercises in cooperation with the Faculty of Chemistry - 23.11.2019
- *Optical and electron microscope*; classes for the pupils from the High School no V in Torun, Faculty of Mathematics, Physics and Informatics, University of Gdansk, laboratory exercises - 13.02.2020
- *Luminescence at a crime scene*; „Talented from Pomerania”, on-line lecture - 21-25.09.2020
- *What shines in a spectroscopic laboratory?*; „Talented from Pomerania”, on-line laboratory exercises - 21-25.09.2020
- *A journey through the world at a nano scale*; Faculty of Chemistry, University of Gdansk, invited lecture - 01.2021
- *Physics Olympic Circle meetings* for high school pupils within the „Talented from Pomerania” program, Faculty of Mathematics, Physics and Informatics, University of Gdansk, IV-VI 2021, II-V 2022
- *Luminescence in forensic sciences*; classes for the pupils from the High School of Individual Programs on the occasion of Teacher's Day, Faculty of Mathematics, Physics and Informatics, University of Gdansk, lecture, X 2021
- *Optical refractive index – laboratory exercises; classes for high school pupils*, Faculty of Mathematics, Physics and Informatics, University of Gdansk, laboratory exercises - 05.03.2022
- *Following the breadcrumbs: light for detectives*; classes for high school pupils, Faculty of Mathematics, Physics and Informatics, University of Gdansk, laboratory exercises - 26.03.2022
- *Trunk of physical miscellanea*; classes for junior high school pupils, Faculty of Mathematics, Physics and Informatics, University of Gdansk, laboratory exercises - 02.04.2022
- *Microscopy, Hydrogen cells, photovoltaics*; classes for the pupils from the Academic High School no 1 in Gdynia, Faculty of Mathematics, Physics and Informatics, University of Gdansk, lecture - 23.05.2022, laboratory exercises - 27.05.2022
- *Riddles and puzzles in a spectroscopic laboratory and Microscopy and spectroscopy in forensic sciences*; classes for junior high school and high school pupils, „Talented from Pomerania”, Faculty of Mathematics, Physics and Informatics, University of Gdansk, lectures - 19-28.09.2022

Doctoral dissertations

- Associate Promoter in the doctoral degree conferment procedure of Ms Aneta Lewkowicz
Thesis title: Spectroscopic properties of hybrid materials doped with organic dyes
Scientific degree: doctor of physical sciences in the field of physics
Defense date: 12.03.2015, distinction awarded to dissertation
- Associate Promoter in the doctoral degree conferment procedure of Ms Michalina Walas
Thesis title: Fabrication, structure and luminescent properties of oxide glasses and tellurium glass-ceramics doped with rare earth ions
Scientific degree: doctor of physical sciences in the field of physical sciences

Defense date: 04.12.2020, distinction awarded to dissertation

- Associate Promoter in the doctoral degree conferment procedure of Ms Elżbieta Adamska
Thesis title: Synthesis, study of the structure, and selected spectroscopic properties of new modified core-shell nanomaterials
Scientific degree: doctor of science and natural sciences in the field of chemical sciences
Defense date: 28.09.2022, distinction awarded to dissertation
- Associate Promoter in the doctoral degree conferment procedure of Ms Agnieszka Schlichtholz
Doctoral School, 2020

Master theses

- Master thesis supervisor of Ms Ada Mendel
Thesis title: Spectroscopic properties of fluorescent dyes in hybrid materials doped with silver nanoparticles; 2016
- Master thesis supervisor of Ms Aleksandra Dziubek
Thesis title: Sensitive detection of biologically active individuals on plasmonic platforms; 2016
- Master thesis supervisor of Ms Adrianna Kocińska
Thesis title: Valrubicin detection on plasmonic platforms; 2017
- Master thesis supervisor of Ms Urszula Łozowska
Thesis title: Fluorescence conformational study of proteins in systems with a controlled degree of order; 2017
- Master thesis supervisor of Ms Adrianna Józefoska
Thesis title: Spectroscopic properties of Valrubicin; 2018
- Master thesis supervisor of Ms Karolina Jankowska
Thesis title: Study of the aggregation process of Nile Red - a sensitive fluorescent probe in solutions; 2018
- Master thesis supervisor of Mr Jakub Kniter
Thesis title: Application of the nonradiative electron excitation energy transfer phenomenon to activity studies of the MMP-9 enzyme; 2020
- Master thesis supervisor of Ms Natalia Jankowska
Thesis title: Nonradiative electron excitation energy transfer in donor-acceptor systems diffusely placed in MCM-41; 2020

Bachelor theses

- Bachelor thesis supervisor of Ms Adrianna Józefoska
Thesis title: Spectroscopic properties of medicines; 2016
- Bachelor thesis supervisor of Mr Jakub Kniter
Thesis title: Detection of the MMP9 enzyme on platforms; 2018
- Bachelor thesis supervisor of Ms Natalia Kulwikowska

- Thesis title: Application of the OLYMPUS IX73 fluorescence microscope to visualize selected samples; 2018
- Bachelor thesis supervisor of Ms Natalia Jankowska
Thesis title: Activity determination of the MMP-9 enzyme in a donor – peptide – acceptor system; 2018
 - Bachelor thesis supervisor of Ms Patrycja Bielska
Thesis title: Absorption phenomenon investigation of molecules of biological and medical importance, in thin layers; 2018
 - Bachelor thesis supervisor of Ms Katarzyna Zadrzyńska
Thesis title: Application of electron microscopy in studies of biological samples and medical products; 2020

List of implemented didactic projects:

- Project of the Foundation for Didactic Initiatives of the University of Gdansk no 500/5200-S650-17
Title: Introducing students of Forensic Science to modern research methods from the field of science
Realization period: 2017, project completed
Function: Principal Investigator

Within this project I created a set of 14 instructions for laboratory exercises for Forensic Sciences students at criminalistics specialization

- Project of the Foundation for Didactic Initiatives of the University of Gdansk no 500-K204-S650-20
Title: Modern acoustic methods in a didactic laboratory
Realization period 2020, project completed
Function: Principal Investigator

Within this project I created a set of 4 instructions to acoustics laboratory exercises for Medical Physics and Forensic Sciences students

7. Apart from information set out in 1-6 above, the applicant may include other information about his/her professional career, which he/she deems important.

In 2007, I defended my doctoral dissertation, written under the supervision of Prof. dr hab. Piotr Bojarski, entitled "Migration of electron excitation energy in uniaxially oriented polymers". In my thesis, I presented an accurate description of the phenomenon of energy transfer in a single-component system in ordered polymers. Another key achievement that I presented in my thesis was a precise method, developed by me, for determining the angle between the directions of the electron transition moments of elongated fluorophores.

In 2010 - after coming back from year and a half research internship in the laboratory of prof. A. Douhal at the University of Castilla La Mancha - I won a competition for a scientific and teaching assistant professor position at the Division of Molecular Spectroscopy (currently Division of Biomaterials and Medical Physics) at the Institute of Experimental Physics of the University of Gdansk. And in this team, led by prof. dr hab. Piotr Bojarski, I have been continuing my research dedicated to the excitation energy transfer phenomena in a range of materials, such as polymer films or porous hybrid matrices.

Since 2010, I have expanded my research interests to include also phenomena such as molecular fluorescence enhancement using plasmonic platforms, interactions of biologically active molecules and medicines with nanomaterials or dyes aggregation in hybrid matrices.

Plasmonics, which is these days of a really extensive interest, is the field of considerable part of my scientific achievements. Although I do not include my works on plasmonics in the scientific achievement constituting the base of my habilitation procedure, I still consider them very important from the point of view of studies on amplification of signal emission from various fluorophores. Most of the fluorophores of potential applications has, unfortunately, a moderate only or not very high quantum emission efficiency. Because of this fact, the fluorescence background signal often causes severe problems during investigations of typical, naturally occurring systems. Still another difficulties to overcome in studies related to fluorophores application are the photodegradation of fluorophores exposed to excitation light (mainly the molecules in excited states undergo photodegradation) or measurements of fluorescence emitted by very thin surface layers – that are vastly desirable in biosensing.

My research was mainly focused on fluorescence signals enhancements on plasmonic platforms, which were manufactured by appropriate deposition of silver or gold nanoparticles, or core-shell nanostructures (Ag@SiO₂) on semitransparent silver or gold mirrors. One of the nanoparticles deposition techniques here is direct application of a metal colloid solution on a mirror surface and evaporation of the solvent (the so-called self-assembling), another method is the eutectic growth of nanostructures on glass substrates.

Publications [**14, 22, 23, 28, 29, 32, 35, 41** in attachment 4B] show the results of research dedicated to the preparation of plasmonic platforms and the data obtained while exploiting the fabricated platforms in sensitive fluorescence measurements. Enhancing the sensitivity of fluorescence measurements enables increasing the sensitivity of detection of certain vitamins, oncological drugs, trace amounts of chemical compounds, enzyme activities, examining intermolecular processes occurring in the surface layers of substances/samples, boosting the emission efficiency of new inorganic materials used for the production of light sources, improving photostability of samples with light-sensitive fluorophores.

Some of the plasmonic platforms I designed enhanced the fluorescence signals from the examined molecules up to 50 times, and additionally - thanks to the employment of Ag@SiO₂ core-shell nanostructures - the unfavorable phenomenon of oxidation of silver nanoparticles was eliminated, which extended the applicability time of the plasmonic platforms.

I plan to combine the discussed above investigations with the research on the use of excitation energy transfer in biosensing. Although the so far obtained by me qualitative results delivered by merge of these two research streams are promising, yet developing a useful model of plasmon-enhanced energy transfer still requires overcoming of several difficulties.

Since the beginning of my employment at the University of Gdansk, I have been collaborating with scientists from a range of other research centers in Poland and abroad:

- prof. Ignacy Gryczyński, prof. Rafał Fudała,
Department of Microbiology, Immunology and Genetics,
University of North Texas Health Science Center, USA,
cooperation related to FRET phenomenon, enzyme activity investigations, plasmonics [1, 2, 9, 10,19, 20- 23, 26, 29, 33, 35, 36 in attachment 4B (list of all publications after obtaining the PhD degree)]
- prof. Sabato d’Auria,
Institute of Food Sciences, National Research Council, Italy,
cooperation on the detection of toxins based on the technique of fluorescence signals enhancement on plasmonic surfaces and on increasing of the range of the FRET process [6,14 in attachment 4B (list of all publications after obtaining the PhD degree)]
- prof. Leszek Kułak,
Faculty of Applied Physics and Mathematics, Gdansk University of Technology,
cooperation regarding exploitation of the Monte-Carlo simulations to studies of the electron excitation energy transfer phenomena [1, 2, 5, 6, 9, 12, 17, 18, 20, 33, 39, 43, 45 in attachment 4B (list of all publications after obtaining the PhD degree)]
- dr hab. Barbara Kościelska, prof. PG, dr hab. inż. Jakub Karczewski, dr Marcin Łapiński,
Faculty of Applied Physics and Mathematics, Gdansk University of Technology,
cooperation related to research on new materials for plasmonic studies and on properties of glasses and ceramics doped with rare earth ions [21, 24, 25, 30, 31, 32, 37, 38, 42, 44, 46, 47 in attachment 4b (list of all publications after obtaining the PhD degree)]
- prof. dr hab. Tomasz Martyński,
Faculty of Materials Engineering and Technical Physics, Poznan University of Technology,
cooperation regarding the study of the properties of perylene derivatives in polymers and Langmuir-Blodgett layers [27, 34 in attachment 4B (list all publications after obtaining the PhD degree)]
- prof. dr hab. Wiesław Wiczak, dr hab. Beata Grobelna, prof. UG, prof. dr hab. inż. Tadeusz Ossowski, dr hab. Paweł Niedziałkowski,
Faculty of Chemistry, University of Gdansk,
cooperation regarding the synthesis of materials for research on plasmonics, FRET phenomena and porous matrices [5, 7-12, 15- 18, 20, 22, 23, 26, 29, 33, 35, 36, 39, 41, 45 in attachment 4B (list of all publications after obtaining the PhD degree)]

Listed below are the completed research projects, other than those stated in point II.9 of the attachment 4A, awards and scholarships received, including those related to implementation of research and teaching works and tasks, training courses in which I participated (some of this information has been already mentioned in the sections above).

Projects

1. Project NCN MINIATURA1 no 2017/01/X/ST4/00542
Title: Concentration characteristics of the anticancer drug – Valrubicin
Realization period: 04.10.2017-03.10.2018, project completed
Funding amount: 40 700 PLN
Function: Task Leader
2. Small Grant Scheme – UGrants realized at the University of Gdansk as part of the Research University Excellence Initiative program, competition konkurs UGrants-first no 533-K000-GF10-21
Title: New sources of white light at the nanoscale on core-shell structures
Realization period: 01.01.2021-15.12.2021, project completed
Function: Principal Investigator
3. University of Gdansk Research Grant no BW-538-5200-0634-11
Title: Luminescence spectroscopy of Ivabradine and products of its metabolism
Realization period: 01.01.2011-31.12.2011, project completed
Function: Principal Investigator
4. University of Gdansk Research Grant no BW-538-5200-0980-12
Title: Method for determining local concentrations in porous hybrid materials
Realization period: 01.01.2012-31.12.2012, project completed
Function: Principal Investigator

List of awards and scholarships received, including those related to implementation of research and teaching works and tasks

Before obtaining the PhD degree (period: 2001-2006)

1. First-rank Rector's Team Award for a series of publications on the photophysical properties of di-methylaniline derivatives in solutions and polymers and the energy transport processes in polymers, 2004

After obtaining the PhD degree (period: 2007-2023)

1. Research Maria Skłodowska-Curie scholarship under the 7th European Union Framework, Departamento de Química Física, Universidad de Castilla-La Mancha, Toledo, Spain, 2008 – 2009
2. Medal of the National Education Commission, card no 168727, 2019
3. Third rank Rector's Team Award for a series of papers in molecular physics, 2007
4. Second rank Individual Rector's Award for a series of six publications in renowned scientific journals with a high Impact Factor (IF), listed in the Journal Citation Reports (JCR) database, 2018
5. Indywidualna Nagroda Rektora stopnia drugiego za całokształt osiągnięć naukowych i dydaktycznych, 2023
6. Scholarship for young doctors within the project „We educate the best - a comprehensive program for the development of doctoral students, young doctors and academic teaching staff of the University of Gdansk” implemented under the Human Capital Operational Program, co-financed by the European Social Fund, 2011

List of training courses:

1. Training on modern experimental methods in Raman spectroscopy, 2010
2. Training on fundamentals of LabView programming, 2010
3. Training on LabView image processing, 2010
4. Training on radiological protection and handling of ionizing sources in medicine, industry and laboratory, 2013
5. Spectro-Lab Seminar: Molecular spectroscopy techniques: new ideas, advanced solutions, modern research equipment, experience exchange, Warsaw, 2017
6. Training of the Prof. Dr. Jan Sehn Institute of Forensic Expertise in Krakow: Forensic traces and their significance in pre-trial proceedings, Krakow, 20.10.2017
7. Training on modern laboratory methods for physics teachers, County School Complex no 2 in Wejherowo, 18.05.2019
8. IT training in creating e-learning content, 10-12.03.2021, 24-25.03.2021 (40 h), on-line, MSTeams Platform
9. VIII National Tutoring Congress, Wrocław, Collegium Wratislaviense, 24-26.09.2021
10. Training on: Working with students with mental health difficulties as part of the project: „Accessible UG - a comprehensive program to eliminate barriers to access to education for people with disabilities”, on-line, 7-8.06.2021
11. Training course at the University of North Texas, Health Science Center, Fort Worth, whose supervisor on the US side was Mr. Prof. Rafal Fudala, director of the Drug Research Laboratory. The training covered an introduction to the latest techniques in the field of the synthesis and applications of micellar systems for transporting anticancer drugs in living organisms -13-21.06.2022r. (Erasmus +; KA107)

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(Applicant's signature)