

## 1. Principal investigator (PI), title of research project, site of research, duration of project (months)

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Title: Taming photochemistry: Controlling excited state dynamics for molecular devices (TaCo)  
Site of research: Nanoscience center  
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Duration: 72 months

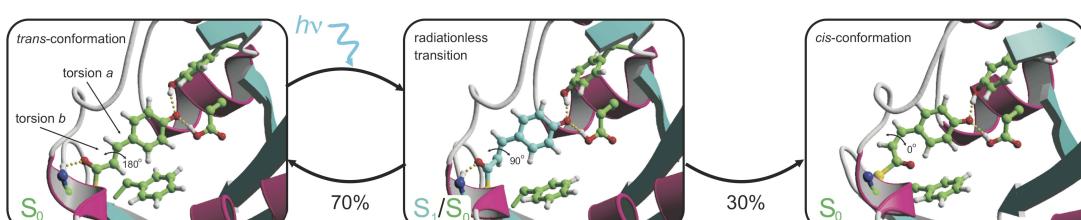
## 2. Background

Interaction between biology, physics and chemistry presently provides a window into the exciting new era of bio-inspired nanotechnology. In particular the photobiological processes of vision and photosynthesis, in which sunlight is used as the source of energy to bring about highly selective and efficient chemical reactions, provide valuable templates to create tools for nanotechnology, biomolecular imaging, information technology and renewable energy.

Mimicking of these biological processes requires a thorough understanding of the underlying molecular dynamics. As the relevant time and spatial resolution are notoriously hard to access experimentally it is difficult to get the required information by experiment alone. Computer simulations, on the other hand, can provide such information, and are thus perfectly suited to complement experiments in unraveling the atomistic details of photochemical processes in biological systems.

To follow the dynamics of photo-activated processes in biological systems, we have developed and applied an advanced simulation technique to compute atomistic trajectories of such processes,<sup>1</sup> as illustrated in Fig.1. From the simulations, one can identify the chromophore-protein interactions that control the photochemical process. I propose to apply such knowledge for designing new systems, in which we can steer the excited state dynamics by simple means, such as chemical substitutions, or external electric fields. Thus, we will design and test, both by computations and experiments new systems that share the functionality, but not the complexity of the protein systems.

The processes we will try to bring under our control are photo-isomerization and excitation energy transfer, both of which are important processes in photobiology. Controlled photoisomerization is essential for developing optical switches and molecular motors. Our aim in controlling excitation energy transfer is to validate an alternative theory for understanding this process fundamentally. Ultimately, controlled excitation energy transfer can be used for sensitizing or tuning the action spectrum of the isomerizing devices and other systems.



**Figure 1:** snapshots from QM/MM simulation of photoisomerization in Photoactive Yellow Protein.<sup>2</sup> Upon photo-excitation, the double bond (torsion *b*) rotates by 90°. After radiation-less decay, the chromophore relaxes into the *cis* conformation with a quantum yield of 0.3.

### 3. Objectives

We want to demonstrate that it is possible to **use the principles of photobiology to create molecular devices**, and we will focus on **photo-isomerization**, where light absorption triggers a rotation around a chemical bond, and **excitation energy transfer**, where light is absorbed by one chromophore and emitted or used by another. By controlling these processes at a molecular level through either chemical substitutions or electric fields, as in photobiology, we will **create electro-chromic devices, optical switches, and molecular motors**. These new bio-inspired systems will be developed in three stages: (i) computational design, (ii) organic synthesis, and (iii) spectroscopic validation.

The requirement for designing molecules on a computer is that the process of interest can be described in terms of nuclear dynamics on electronic potential energy surfaces. Since excitation energy transfer is described on the basis of empirical theories (Förster and Dexter) that cannot be used to design new systems, we will also **develop a general theoretical framework for excitation energy transfer** in terms of potential energy surfaces.

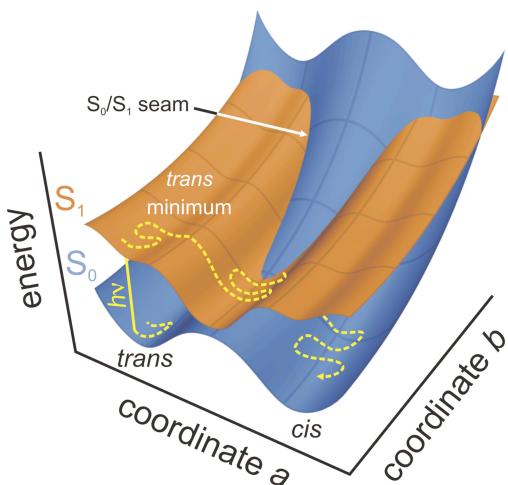
In order to carefully validate the results of the simulations, we also will **develop new techniques for computing time-resolved spectra** that we can compare directly to the raw spectroscopic data.

Summarizing, the main objectives in this project are:

1. To extract spectroscopic data from MD trajectories;
2. To control photoisomerization in molecules;
3. To develop and validate new theory for excitation energy transfer; and
4. To control excitation energy transfer between chromophores.

#### 3.1 Hypotheses

The central mechanistic feature in photochemical reactions is the intersection seam between the potential energy surfaces of the excited ( $S_1$ ) and ground state ( $S_0$ , Fig. 2). Any point on this seam provides a funnel for efficient radiation-less decay to the ground state. Just as a transition state separates reactants and products in ground state chemistry, the seam separates the excited state branch from the ground state branch in a photochemical reaction (e.g. photo-isomerization, or excitation energy transfer, see below). The crucial difference, however, is that while a transition state connects a reactant to a *single* product via a *single* reaction path, the seam connects the excited state reactant to *several* products on the ground state via *several* paths.



**Figure 2:** Photochemical reaction pathway (dashed line). After photon absorption, evolution takes place on the excited-state potential energy surface until the system hits the  $S_1/S_0$  intersection seam. There a radiationless transition takes place to the ground-state. After the decay, the system continues evolving on the ground-state surface.

The outcome of photochemical reactions can be steered by controlling the access to the seam. This can be achieved by altering the topologies of the surfaces and seam, through electrostatic and steric interactions. In the Photoactive Yellow Protein (PYP) photoisomerization of the chromophore is enhanced by stabilization of the seam through electrostatic interactions with the protein environment.<sup>2</sup> In Green fluorescent protein (GFP), fluorescence is enhanced by suppression of competing decay channels through steric hindrance.

Alternatively, the outcome can be controlled by steering the dynamics of the wave-packet on S<sub>1</sub> towards a specific part of the seam. This strategy is often referred to as optimal control.<sup>3</sup> It focuses on the optimization of the radiation source rather than the molecule.

We will focus on manipulating the shape of the potential energy surface by optimizing the molecule or applying external electric fields. Since evolution has followed this strategy as well, most of the inspiration for designing new photoactive systems will come from unraveling how proteins have evolved to mediate their photochemistry.

#### 4. Research methods and material, ethical issues

The research is subdivided into four sub-projects to be carried out in different labs, specialized in organic synthesis (Prof. Pihko), ultra-fast spectroscopy (Prof. Ihalainen and Prof. Pettersson) and computational chemistry (Prof. Häkkinen and myself).

##### 4.1 Computer simulations of photochemical processes

The established computational approach to photochemical problems is to model the electronic structure of isolated chromophores at the highest possible level of *ab initio* theory and characterize reactant, product and intersection geometries. We have developed an alternative protocol for simulating photochemical reactions in biomolecular systems.<sup>1,2</sup> Our approach is different from the established approach in two main respects. First, in contrast to the conventional quantum chemistry approach, molecular dynamics (MD) trajectories at room temperature are computed, rather than stationary points (essentially 0 K), which is not only more realistic, but also avoids the choice of an *a priori* reaction coordinate. Second, while most theoretical studies on photo-reactivity still concentrate on isolated chromophores, we include the protein environments explicitly in our simulations.

In our scheme, a multi-configurational quantum mechanical description (CASSCF) is used to model the electronic rearrangement for those parts of the system that are involved in the absorption of the photon, usually the chromophore. For the remainder, typically consisting of the apo-protein and the solvent, a simple force field model suffices. The interactions in the system are thus computed within a hybrid quantum/classical framework (QM/MM). Forces are calculated on-the-fly, and a surface hopping algorithm is used to model the excited state decay (Fig. 2). The validity of our approach has been demonstrated in several applications on photoactivation of photoreceptor proteins (Fig. 1),<sup>2,4</sup> on photo-switching of fluorescent proteins,<sup>5</sup> and on photochemical reactions in DNA.<sup>6</sup> Based on these successes, I believe that the simulation protocol provides a promising basis for rational design of photochemical devices, as well as testing the functionality of these new systems prior to the much more time- and cost-intensive chemical synthesis.

## 4.2 Computational Spectroscopy

To verify whether systems that function in simulations, also work in reality, we will use spectroscopy in the visible and mid-infrared regions. To facilitate interpretation of these experiments we will first compute spectra from our molecular dynamics trajectories. We will distinguish between stationary spectra of stable or metastable intermediates, and time-resolved spectra that follow structural changes during the photochemical process. Because of the approximations underlying the simulations we cannot expect to get excitation energies accurate enough for a quantitative comparison to experiment. Therefore we will compute and compare difference spectra instead, defined with respect to the stationary ground-state spectrum.

### 4.2.1 UV/Vis spectroscopy

To simulate UV/Vis spectra, we calculate at every frame of the trajectory the energies of several electronic states. Since no gradients are required, we have several methods at our disposal, such as CASPT2, CIS(D), TD-DFT, CC2, or even the fast semi empirical ZINDO method. In each frame, the gaps between these energies correspond to either excited state absorption or stimulated emission frequencies. Averaging over many frames yields a stationary spectrum, while averaging time-dependent spectra over many trajectories yields a pump-probe or fluorescence up-conversion spectrum. By comparing the spectra to experimental spectra, we can validate the dynamics in the simulations.

### 4.2.2. IR spectroscopy

The established approach for computing anharmonic IR spectra from MD simulations is to Fourier transform the dipole auto-correlation function.<sup>7</sup> As we are interested in difference spectra, we only need the IR frequencies of the atoms inside the QM subsystem, and therefore can leave out the solvent from the analysis. However, to reach spectral resolution below 1 cm<sup>-1</sup>, trajectories of several tens of picoseconds are required. Since for accurate QM/MM simulations, such timescales are beyond reach, we have recently applied auto-regressive (AR) filter algorithms to identify periodic motions in MD trajectories with a higher resolution.<sup>8</sup> Since AR filter methods are parameter-based, we have to find the optimal parameters first. To do so, we numerically simulate IR spectra using the normal mode frequencies of an isolated model system (*i.e.* the QM subsystem) to which we add random (white) noise. Since the number of peaks is known beforehand, the parameters of the AR filter can be optimized to reproduce the normal mode spectrum from the noisy data. With these parameters we can compute IR spectra from short trajectories. The stationary IR spectrum is obtained by averaging these spectra.

An alternative approach will be developed for computing also **time-resolved IR spectra** from non-equilibrium excited state dynamics trajectories. To avoid using quantum mechanics for the nuclear degrees of freedom, we will only focus on a few important IR-active modes (*e.g.* C=O stretch)) and introduce a number of approximations. As in standard Normal Mode Analysis (NMA), we will assume that the QM/MM potential energy surface is harmonic. We also assume that time-dependent interactions with the environment only change the width of the harmonic potential (force constant), but not the character of the mode. Thus, the modes of interest will be identified in the isolated systems through NMA. The change in force-

constant of this mode due to interaction with the environment is obtained by fitting a harmonic function to the potential energy landscape along this mode. By analyzing the force constant, and dipole derivative in each frame of the trajectory, we can compute the evolution of the IR frequency and intensity of the selected modes in response to the excited state dynamics. The time-dependent shifts of the selected IR peaks can be compared to pump-probe IR spectra.

#### 4.2.3 Validation

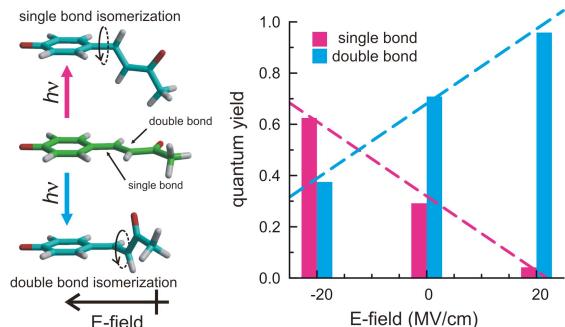
In collaboration with the Ihlainen group we will apply the new methods on phytochrome from *Deinococcus radiourans*. This photoreceptor contains a chromophore that undergoes photo-isomerization to yield an activated state, the structure of which is hitherto unknown. Goal of this validation project is therefore not only to validate our simulation methods, but also to establish the structure of this state. We will thus perform QM/MM simulations of this protein (PDB-id: 1ZTU)<sup>9</sup> and compute spectra from the trajectories. These spectra will then be compared the experimental data measured by the Ihlainen group. In parallel, we also compute spectra from our QM/MM simulations of PYP and compare these to the experimental data available in the literature as well as new data by Prof. Groot in Amsterdam.

If successful, the developments proposed here will greatly contribute to interpreting pump-probe data of both existing systems, as well as the new systems that we will develop in the course of the project. All software developments will immediately be made available to the community through the MD software package Gromacs, of which I am one of the official developers.

### 4.3 Controlling photo-isomerization

We want to control specificity, efficiency and quantum yields of isomerization in chromophores by changing their photophysical properties by means of external electric fields and chemical substitutions.

#### 4.3.1. Electric fields



**Figure 3:** a static electric field controls the ratio between single and double bond photo-isomerization in a PYP chromophore analogue.

The excited states of many biological chromophores exhibit a strong charge transfer character, so that the dipole moments of the excited and ground state differ significantly. As a consequence, the charge distribution inside the protein can preferentially stabilize one electronic state with respect to the other and thereby steer the dynamics in the excited state. As we have shown for the PYP<sup>2</sup> and asFP595 chromophores,<sup>5</sup> such selective electrostatic stabilization can even induce surface crossings between the ground and excited state and thereby enhance radiationless decay. Thus, in these proteins, the photochemistry is controlled by *internal* electric fields that are effectively static on the timescales of the reaction.

These observations suggest that also *external* electric fields can be used to control photo-isomerization. To test this idea, we performed excited state dynamics simulations of a PYP chromophore analogue (pCK<sup>+</sup>) in an external electric field (Fig. 3). By adjusting direction and strength of the field, we were able to control both

selectivity (*i.e.* which bond isomerizes) and efficiency (excited state lifetime) of the isomerization process.<sup>10</sup>

The first step in this sub-project is to confirm these findings experimentally. We will covalently attach the chromophores to mono-layer-protected gold nanoparticles.<sup>11</sup> These nano-particles are multivalent redox species, and their total charge can be manipulated with (macroscopic) electrodes.<sup>12</sup> Thus, we can control the electric field at the chromophores in the experiments. Because the nano-particles are soluble, charged chromophore will pose no difficulties. Finally, crowding of the linkers may facilitate alignment of the chromophores to the field, and reduce the dielectric response.

The Pettersson group has already performed spectroscopic measurements on these nanoparticles,<sup>13</sup> while the Häkkinen group were among the first to perform electronic structure calculations on the particles.<sup>14</sup> Furthermore, the existing collaboration between Pettersson and Kornberg (Stanford) guarantees availability of the particles.

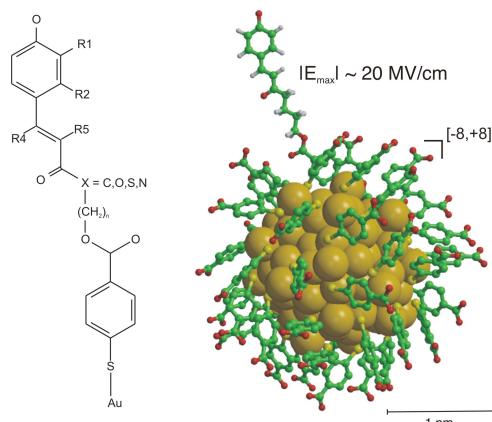
Prior to the experiments, we will perform QM/MM simulations of the complete system (Fig. 4) and investigate the excited state dynamics at different oxidation states of the nanoparticle. The nanoparticle will be modeled by a force field, which we will develop for all oxidation states in collaboration with Häkkinen and Akola. In particular, we will investigate the effect of different linkers as well as small substituents on the chromophore (*i.e.*, R1 to R5, Fig. 4).

The most promising systems will be synthesized in the lab of Pihko. Different spectroscopic techniques will be applied to investigate the effect of the oxidation state of the gold particle on the photo-isomerization of the chromophore. In particular, the quantum yield of double and single bond isomerization (possibly detectable after substitution on R2), and excited state lifetime are needed for validating the theoretical predictions. We may also test different biological chromophores, such as retinal and hydroxybenzylidene-imidazolone, the chromophores in rhodopsin and green fluorescent protein, respectively. By introducing substituents that enhance the difference in dipole moment between the ground and excited state, we will try to create chromophores whose access to the conical intersection is controlled by the field.

All molecules will be screened in computer simulations and the most promising systems will be selected for experiment. Feedback from experiment will help to further improve these systems. If we can succeed in enhancing sensitivity to the field to such extent that even in standard capacitors (up to  $2 \text{ MVcm}^{-1}$ ) we can control the access to the seam, these chromophores may find application in display technologies as a low-energy alternative for the organic light emitting diode (OLED) displays.

#### 4.3.2. Chemical substitution

The next, more ambitious goal is to design systems, in which photo-isomerization is controlled by internal interactions. The ultimate goal is to design systems that undergo unidirectional isomerization repeatedly upon photo-excitation. Such systems may act



**Figure 4:** Gold nanoparticle coated with a chromophore. the electric field at the chromophore is controlled via the charge state of the gold particle.

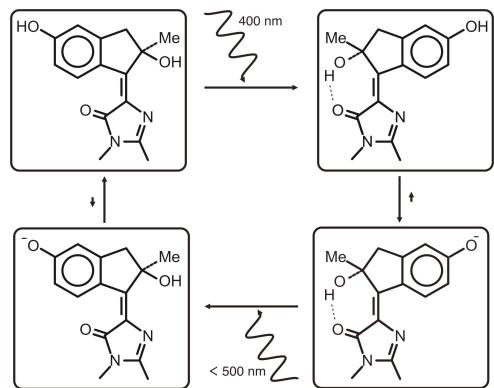
like motors that convert light into directional motion, similar to the ones pioneered by Feringa and coworkers.<sup>15</sup>

First we try to develop optical switches that can isomerize with high efficiency upon photo-excitation. Because such switch has recently been designed on the basis of QM calculations,<sup>16</sup> the risk of this project is moderate. In that switch, however, the absorption spectra of the two isomers strongly overlap, which could limit its practical use. We will try to increase the difference of the two spectra in our switches by coupling photo-isomerization to changes in protonation state. Such coupling lies at the basis of photo-activation in PYP and proton pumping in bacteriorhodopsin, where the photo-isomerization initiates proton transfer reactions.

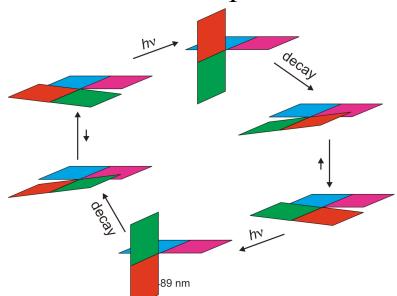
As in PYP, an isomer specific  $pK_a$  shift of titrating groups can be induced if the isomerization breaks intramolecular hydrogen bonds or conjugation. This concept is illustrated for a derivative of the GFP chromophore in Fig. 5. Density functional theory computations on this molecule show that breaking the internal hydrogen bond upon isomerization indeed increases the  $pK_a$  of the phenol group. We will design switches that fulfill these requirements and test their functionality by computer simulations. The most promising systems will be selected for experiment.

Particular challenging is creating so-called reversibly switchable fluorescent molecules that can be photo-switched between a dark and fluorescent state reversibly. The requirement for such functionality is that there is one isomeric state has a sufficiently high isomerization barrier in the excited state to block isomerization and allow fluorescence instead. This can again be achieved by isomer specific protonation states. In the example in Fig. 5, the barrier for isomerization from trans (bottom right) to cis (bottom left) is higher due to the internal hydrogen bond. Since reversibly switchable fluorescent molecules are the backbone of the high-resolution microscopy technique RESOLFT,<sup>17</sup> developing such molecules is a high risk/high gain project.

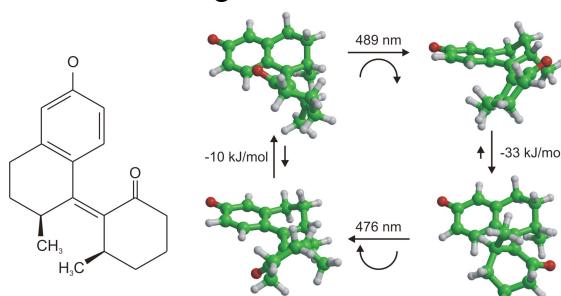
Equally high risk/high gain is the development of light-driven molecular motors. Based on our experience with the chromophore of PYP, we will try to achieve unidirectional rotation in this chromophore by introducing chiral substituents. Such substituents must pre-twist the ground state configuration of the double bond in the



**Figure 5:** HBDI-mimic (GFP chromophore). The  $pK_a$  of the phenol is 1  $pK_a$  unit higher in the cis (left) than in the trans (right) isomer based on B3LYP/6-31G\* calculations.



**Figure 6:** unidirectional rotation upon photo-isomerization can be achieved via pre twisting the molecule in the most stable ground state minima, see Fig. 7.



**Figure 8:** possible implementation of the concept in Fig. 6 in a motor based on the PYP chromophore. Ground state geometry optimizations were performed at B3LYP/6-31G\* level, while the excitation wavelength were obtained at CIS(D)/6-31G\* level.

same direction through steric interactions and bias the photo-isomerization to occur in a single direction through photo-excitation (Fig. 6). Because such asymmetric interactions may also inhibit a successful photo-isomerization of the double bond, the challenge is to introduce these substituents while keeping a high enough isomerization quantum yield to extract work. One of our current ideas is shown in Fig. 8. The energy difference between the ground state minima both in the cis, as well as in the trans configurations ensures that the species absorbing the photon will always isomerize clockwise. After testing the motors by computation, we will try to synthesize the most promising compounds and use spectroscopy to validate whether these systems undergo uni-directional rotation upon stimulation with light.

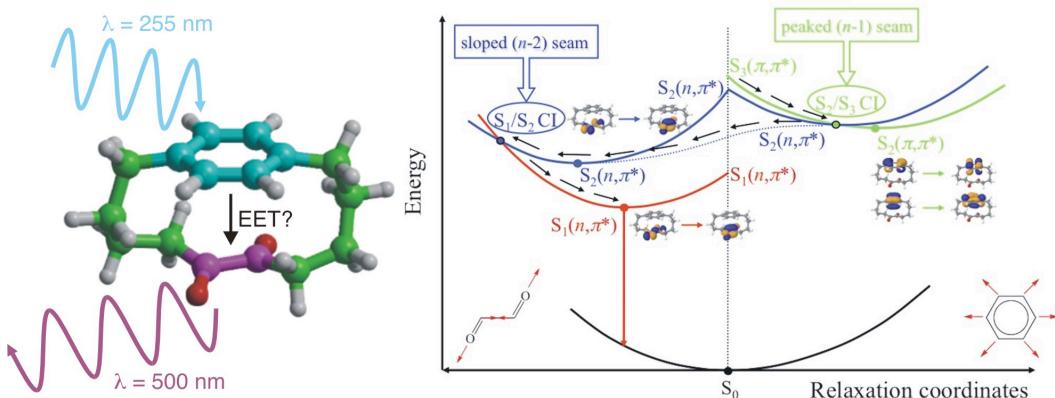
#### 4.4 Controlling Excitation Energy Transfer (EET)

##### 4.4.1 A dynamic view on excitation energy transfer

The aim in this sub-project, which can be carried out in parallel with the other projects by one PhD student, is to demonstrate that EET in bi-chromophoric systems, so-called dyads, can be understood in terms of non-adiabatic nuclear dynamics involving multiple electronic potential energy surfaces. We will focus on the small dyad shown in Fig. 8a, in which excitation at 268 nm causes fluorescence around 480 nm. Dyads of this type have been studied by Speiser et al. who used Dexter theory to explain the very efficient transfer of the excitation from the xylene onto the di-acetyl group of this molecule.<sup>18</sup>

However, CASSCF/CASPT2 computations (Fig. 8b) provide a very different explanation for the observations, which may impact the way EET is understood. In this dyad, there is a conical intersection between the optically active ( $\pi,\pi^*$ )-state on xylene and the second optically-forbidden ( $n,\pi^*$ )-state on di-acetyl. Because this intersection coincides with the minimum on the ( $\pi,\pi^*$ )-state potential energy surface it cannot be avoided (Fig 8b), so that the EET process must occur with a 100% quantum yield. Thus, at least for this molecule, the assumptions underlying Dexter and Förster theories may need to be revised.

To confirm our view, we propose to perform excited state molecular dynamics of this compound to quantify the efficiency and rate with which the dyad relaxes into the fluorescent  $S_1$  ( $n,\pi^*$ )-state. The proposed developments in modeling spectroscopy (4.2), will allow us to predict the changes in spectroscopy while the dyad undergoes



**Figure 7:** Intra molecular EET in dyad (left). CASSCF potential energy curves (right) of the 3 lowest excited states. Relaxation in the  $S_3$  state, localized on benzene (cyan) leads to a conical intersection to the  $S_2$ , localized on the di-acetyl (magenta). Thus, in this system the EET process is well understood in term of non-adiabatic nuclear dynamics. Dotted portion of the curve indicate displacements in other dimensions than the reaction coordinates.

intramolecular EET. These predictions will facilitate the experimental verification.

In the second step, we will synthesize the dyad and perform pump probe UV/vis and IR, as well as fluorescence up-conversion measurements. As the synthesis procedure for such dyads are described in literature,<sup>19</sup> the PhD student will be able to perform the synthesis in the lab of Pihko. In addition, under supervision of Petterson and Ihalainen, the student will also perform the spectroscopy experiments.

If the proposed experiments confirm this dynamic picture, we will go one step further and explore if our description for EET also applies to EET in biological systems. Due to the size restriction of the CASSCF method, we will look into EET between small chromophores. Since in PYP intramolecular EET from tryptophan onto the chromophore has been observed recently,<sup>20</sup> we will study this system. By including the rest of the protein explicitly in our QM/MM computations, we will also explore the effect of the environment on the EET process. Due to their sizes, describing the two chromophores simultaneously at the CASSCF level, is computationally a lot more demanding than before. Therefore, we may have to restrict ourselves to static computations, as we have done on the dyad so far (Fig 8b), instead of dynamics to demonstrate the alternative view on EET. Alternatively, we may resort to more approximate electronic structure methods for optically excited states, such as the approximate coupled cluster CC2 method, time-dependent density functional theory, or the semi empirical OM2 method. After proper benchmarking, we may even be able to use these faster methods to calculate trajectories.

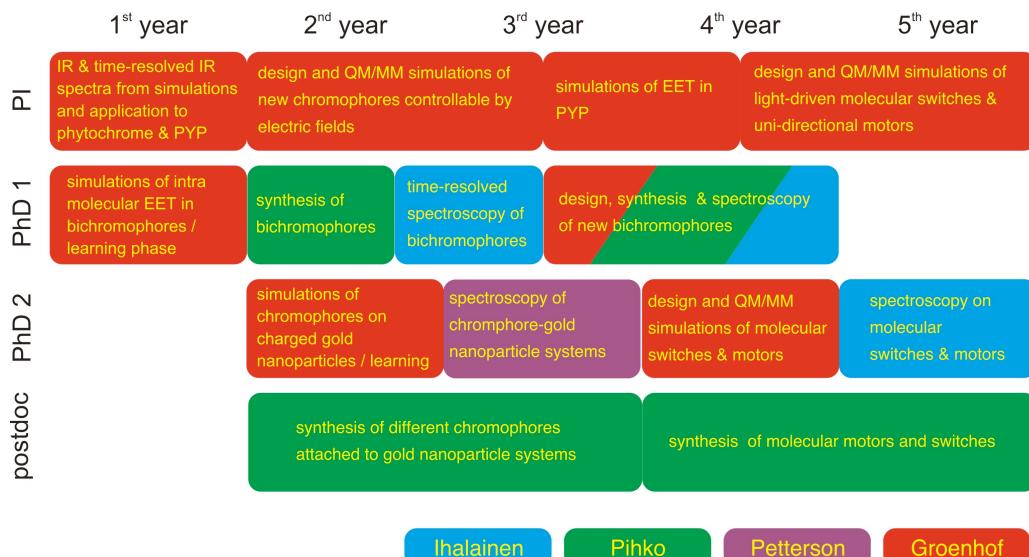
#### 4.4.2. Designing new bi-chromophoric systems

If confirmed, our description of EET in terms of non-adiabatic molecular dynamics opens up the route towards designing new systems. In the dyads, the efficiency of EET is determined by the accessibility to the seams, which we may be able to control by electric fields and substituents. Of particular interest is the effect of the linker in this context. Previous experiments by Speiser have shown that the EET is critically dependent on the length of the linker, but explained this effect by Dexter theory.<sup>18</sup> By repeating MD simulations and experiments on dyads with different linkers, we will try to understand this effect and exploit it to design new dyads with pre-defined efficiencies. Furthermore, we will aim at producing new dyads with custom absorption and emission wavelengths. Eventually, our efforts may lead not only to a better understanding but also a better perspective for engineering EET. The latter will be particularly useful for designing molecular photo-sensitizers, which harvest energy to be used for a photochemical process elsewhere in the system.

#### 4.5 Risks and challenges

Since in this project we use computation as the basis for a synthetic chemistry campaign, a major risk is that these computations are not sufficiently accurate for the problems at hand. There are two ways to minimize this risk. First, we always employ a hierarchical calibration strategy for our computations. All static properties of the chromophores are compared to higher levels of theory, e.g. CASPT2 or RASSCF, in particular, the ordering of the excited states. Second, we will compute spectra and compare these to experiment to further verify the validity of our approach.

Nevertheless, even with a reliable description of the excited state dynamics, it will be difficult, if not impossible, to predict all possible side reactions in both ground and excited states. This is especially problematic for biological chromophores, most of which need the protein environment for chemical stability. For example, hydrolysis or



**Figure 8:** overview of work distribution and time table

auto-ionization can be prevented by the protein. Here, we need chemical intuition and experience instead, which is why we carry out this project together with the Pihko group. Their experience may allow us to work around such issues. Hydrolysis, for example, may be avoided by introducing chemically inert bulky substituents near the nucleophilic centers, whereas auto-ionization may be prevented by hydrogen bonding with the solvent.<sup>21</sup> Nevertheless, even with such experience, we may need a number of trial and error cycles before reaching success.

The worst-case scenario would be that the predictions by theory are neither proven nor disproven. This can happen because the experiment cannot be interpreted, or something unforeseen happens instead of the predicted process. In the latter case, however, a careful structural analysis of the photoproduct by crystallography, and/or NMR, may help elucidate what happened and improve the theory. On the other hand, probing as multi-dimensional time-resolved data (by using for example chromophore replacement or isotope-labeling or other methods) can elucidate further the comparison between theoretical and experimental data.

A design project based on theory is one of the most scrutinizing tests for the employed theory. Thus even if the first results show the theory to be wrong, but we are able to deduce what is wrong, it will lead to both a better understanding of photochemistry, as well as improvement to the theory. This in itself, albeit far from the rather ambitious goals of the project, would be worth pursuing.

## 5. Implementation: timetable, budget, distribution of work

The proposed research can be carried out by two PhD students, one postdoctoral researcher, and myself (PI), and I request funding for these positions. I will be responsible for coordinating the complete project, for the required software development (4.2), and be involved in all design processes (4.2-4.4), as well as study EET in proteins (4.3). I will also supervise all computational work. From the second year on, a post-doctoral researcher will synthesize the designed molecules. Experience is essential, because the compounds need to be made available to the spectroscopic experiments in the shortest possible time. His or her experience is also important for designing the molecules, in which the postdoc will be actively involved. The first PhD student will work on EET in dyads (4.4), and will not only perform the

simulations, but also the experiments, including synthesis. The second PhD student will use computer simulations and spectroscopy to work on steering excited state dynamics by electric fields in the first phase. After completing this phase he or she will continue working on design, simulation and spectroscopy of molecular motors and switches. As the project may appeal to students, I also expect Bsc and Msc students to become involved. A typical contribution from such student will be either a simulations, or experiments on one of the promising systems. The distribution of work over the different labs is shown schematically in Fig 9.

The broad range of tasks requires communication between the groups. Therefore, there will be weekly meetings with all people involved to discuss the progress of the sub-projects, and decide on changes to keep on schedule. Candidate selection will be discussed by all group-leaders and decided on in unison.

In addition to personal costs for a postdoc two PhD students and myself, I request X for three workstations. This equipment is essential to setup and analyze the computations. Since no suitable photodetector is available at the moment to perform fluorescence up-conversion experiments I request X to purchase one. The Ihlainen group will take care of ordering and maintaining this equipment. For consumables, mainly for the proposed experiments, but also to cover publication costs, I request 20,000 € per year. Finally, for visiting international meetings, such as ACS meetings, workshops (Cecam) and schools, which are not only essential to keep an overview of the field, but also to make the field aware of our work by presenting it, I request 10,000 € year for travel, fees, etc. for the team.

year	PI	Postdoc	PhD 1	PhD 2	Consumables	equipment	travel	total
1	56		30		20	?	10	
2	56	50	30	30	20		10	
3	56	50	30	30	20		10	
4	56	50	30	30	20		10	
5	56	50		30	20		10	
total	350	240	120	120	100		50	980

## 6. Research environment

Jyvaskyla is one of the best location for carrying out the project. All required experience and equipment for the proposed experiments are present on-site already, so that I only need to bring in the theoretical contribution, which is my expertise. Very importantly also, is that all group leaders have a strong commitment to the project and have agreed to not only make their equipment available for the experiments, but also supervise the researchers that will carry them out. Moreover, since the topic fits the interests of the NanoScience Center, there will be plenty of opportunities for further collaborations, and exploitation of our results.

The proposed computations will be carried out at in three locations. At the linux cluster that is currently under construction in Jyvaskyla, at the CSC in Espoo, and during the start-up phase, at the 8000+ core Linux cluster at the department of computational biophysics at the Max Planck Institute for biophysical chemistry.

### 6.3 Collaborations

Long-standing collaborations with Prof. Michael Robb (Imperial College London, UK) and Dr. Martial Boggio-Pasque (CNRS, France) exist already and will be essential to develop and refine our simulation protocols. My collaborations with the

other gromacs developers Prof Erik Lindahl, Prof David van der Spoel and Berk Hess, are also important for these developments. An existing collaboration with the group of Prof. Marloes Groot (VU, Amsterdam, NL) on IR spectroscopy of photoactive protein is also important for validating these developments.

## 7. Researcher training and research careers

The PhD students will perform their research in different labs (Fig. 9), and trained in more than one discipline. Since this increases the number of options, I expect their chances to pursue an independent scientific career to be larger. I will prepare the students for such career by actively involving them in writing their papers, refereeing papers and present results at meetings. Via a weekly group meetings and journal club I will train their presentation and literature reading skills. In addition to supervising their research on a daily basis, I will also focus on other skills, such as scientific ethics and fund-raising.

The project also is an opportunity to train myself further and make the transition to anfully independent research group leader. My ambition is to eventually head a group that does both theory and experiments. The current project will allow me to acquire the necessary skills to supervise experiments.

## 8. Expected results and risks

The expected results of this project are: (i) a general understanding of photoisomerization and excitation energy transfer processes; (ii) a set of molecular tools for nanotechnological applications (iii) a thorough means for validation results of excited state dynamics simulations with spectral information; as well as (iv), computer code to compute stationary and time-resolved UV/Vis, IR spectra from MD trajectories. I expect the end-users of the results of my research to be both scientists that use our software and methods, as well as engineers, who may be using the molecules we create for various applications. Examples of applications I can think of are the use of photo-switches for optical 3D-memory storage, of electro chromic switches in displays, of molecular motors attached to surfaces to induce macroscopic motions, or of new photo-sensitizers in photovoltaic devices.

The project may seem ambitious, but the division into smaller independent sub-projects minimizes the total risk. Furthermore, for each sub-project, we already have computational data that support the basic assumptions. Thus, the risk that the computational work will fail is negligible. Both synthesis and spectroscopic techniques are well established, thus the risk that these fails is also minor. An exception may be the projecting involving gold nanoparticles. There may be a strong EET between the chromophores and the gold particle, which would obscure or even prohibit the proposed measurements.

## 9. Key literature or bibliography

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