Quantum Chemical Modeling of Dye-Sensitized Titanium Dioxide

Ruthenium Polypyridyl and Perylene Dyes, TiO₂ Nanoparticles, and Their Interfaces

MARIA J. LUNDQVIST
Dissertation presented at Uppsala University to be publicly examined in Häggsalen, Ångström laboratoriet, Uppsala, Friday, October 13, 2006 at 13:15 for the degree of Doctor of Philosophy. The examination will be conducted in English.

Abstract

Quantum chemical calculations have been used to model dye-sensitized nanostructured titanium dioxide systems that can be used in solar cells for solar energy to electricity conversion. Structural, electronic and spectral properties of isolated dyes and both bare and dye-sensitized TiO₂ have been calculated with density functional theory, providing detailed information about both the separate parts and the dye-TiO₂ interface.

The connection between the geometry, the ligand field splitting and the lifetime of the triplet metal-to-ligand charge transfer (MLCT) excited state has been explored for a series of ruthenium polypyridyl dyes. Moreover, the relative energetics of MLCT and metal centered triplet excited states have been studied for a number of such systems. It was found that small alterations of the polypyridyl ligands can result in significant changes in ligand field splitting and in the energetics of the triplet states.

Attachment of the dyes to the TiO₂ surface is achieved via anchor and spacer groups. The influence of such groups on various properties of the dye and their ability to act as mediators of photo-induced surface electron transfer has been studied. Delocalization of the lowest unoccupied dye orbital onto the spacer and/or anchor group indicates that certain unsaturated groups can mediate electron transfer.

With a combination of methods that enables efficient computations and a scheme for construction of metal oxide clusters, chemical models for bare TiO₂ nanocrystals in the 1-2 nm size range have been developed. The electronic structures show well-developed band structures with essentially no electronic band gap defect states.

Atomistic models of the interface between TiO₂ nanocrystals and Ru(II)-bis-terpyridine dyes, the so-called N3 dye as well as perylene dyes are reported. Electronic coupling strengths, which provide estimates for the electron injection times, are extracted from the interfacial electronic structure and the lowest electronic excitations are calculated.

Keywords: density functional theory, chromophore, nanocrystal, interface, photoexcitation, triplet state, surface electron transfer, electronic coupling strength

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ISSN 1651-6214
ISBN 91-554-6650-8
urn:nbn:se:uu:diva-7141 (http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-7141)
List of publications

I. Structural and spectral investigation of Ruthenium(II) polypyridyl complexes by DFT calculations

II. Ruthenium complexes of bipyridyl(pyridyl)alkane ligands: Effect of methylene or iso-propylene bridge on structural and photophysical properties

III. Calculated optoelectronic properties of Ruthenium tris-bipyridine dyes containing oligophenylenethynylene rigid rod linkers in different chemical environments

IV. Spacer and anchor effects on the electronic coupling in Ruthenium-bis-terpyridine dye-sensitized TiO₂ nanocrystals studied by DFT
M. J. Lundqvist, M. Nilsing, S. Lunell, B. Åkermark, and P. Persson. Accepted for publication in J. Phys. Chem. B. DOI: 10.1021/jp064045j

V. DFT study of bare and dye-sensitized TiO₂ clusters and nanocrystals

VI. Quantum chemical calculations of the influence of anchor-cum-spacer groups on femtosecond electron transfer times in dye-sensitized semiconductor nanocrystals

VII. Calculated structural and electronic interactions of the Ruthenium dye N3 with a titanium dioxide nanocrystal
Related work not included in the thesis

Synthesis and electron transfer studies of Ru-terpyridine based dyads attached to nanostructured TiO$_2$

Electronic coupling calculations for ultrafast photoinduced charge transfer processes from aromatic adsorbates to TiO$_2$ nanocrystals
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Chemical

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<th>Description</th>
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<tbody>
<tr>
<td>TiO₂</td>
<td>titanium dioxide</td>
</tr>
<tr>
<td>py</td>
<td>pyridine</td>
</tr>
<tr>
<td>bpy</td>
<td>2,2'-bipyridine</td>
</tr>
<tr>
<td>tpy</td>
<td>2,2':6',2''-terpyridine</td>
</tr>
<tr>
<td>bmp</td>
<td>[6-(2,2'-bipyridyl)]-(2-pyridyl)-methane</td>
</tr>
<tr>
<td>bm3p</td>
<td>2-[6-(2,2'-bipyridyl)]-2-(2-pyridyl)-propane</td>
</tr>
<tr>
<td>pmp</td>
<td>2,6-di(2-pyridylmethyl)pyridine</td>
</tr>
<tr>
<td>OPE</td>
<td>oligophenyleneethynylene</td>
</tr>
<tr>
<td>E</td>
<td>ethynylene</td>
</tr>
<tr>
<td>Ph</td>
<td>p-phenylene</td>
</tr>
<tr>
<td>Ipa</td>
<td>isophtalic acid</td>
</tr>
<tr>
<td>Bco</td>
<td>bicyclo[2.2.2]octylene</td>
</tr>
<tr>
<td>N3</td>
<td>Ru(4,4'-dicarboxy-2,2'-bpy)$_2$(NCS)$_2$</td>
</tr>
<tr>
<td>Pe</td>
<td>Perylene</td>
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Quantum chemical

<table>
<thead>
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<tbody>
<tr>
<td>MO</td>
<td>molecular orbital</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>TD-DFT</td>
<td>time dependent DFT</td>
</tr>
<tr>
<td>PCM</td>
<td>polarizable continuum model</td>
</tr>
<tr>
<td>HF</td>
<td>Hartree-Fock</td>
</tr>
<tr>
<td>SCF</td>
<td>self-consistent field</td>
</tr>
<tr>
<td>KS</td>
<td>Kohn-Sham</td>
</tr>
<tr>
<td>STO</td>
<td>Slater type orbital</td>
</tr>
<tr>
<td>GTO</td>
<td>Gaussian type orbital</td>
</tr>
<tr>
<td>LDA</td>
<td>local density approximation</td>
</tr>
<tr>
<td>GGA</td>
<td>generalized gradient approximation</td>
</tr>
<tr>
<td>B3LYP</td>
<td>three-parameter hybrid functional</td>
</tr>
<tr>
<td>ECP</td>
<td>effective core potential</td>
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### Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>$\Delta_0$</td>
<td>ligand field splitting</td>
</tr>
<tr>
<td>$S_0$</td>
<td>singlet ground state</td>
</tr>
</tbody>
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### Units

<table>
<thead>
<tr>
<th>Unit</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>nm</td>
<td>nanometer, $10^{-9}$ m</td>
</tr>
<tr>
<td>Å</td>
<td>Ångström, $10^{-10}$ m</td>
</tr>
<tr>
<td>fs</td>
<td>femtosecond, $10^{-15}$ s</td>
</tr>
<tr>
<td>ps</td>
<td>picosecond, $10^{-12}$ s</td>
</tr>
<tr>
<td>ns</td>
<td>nanosecond, $10^{-9}$ s</td>
</tr>
<tr>
<td>μs</td>
<td>microsecond, $10^{-6}$ s</td>
</tr>
<tr>
<td>eV</td>
<td>electronvolt</td>
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### Miscellaneous

<table>
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<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>MLCT</td>
<td>metal-to-ligand charge transfer</td>
</tr>
<tr>
<td>MC</td>
<td>metal centered</td>
</tr>
<tr>
<td>LC</td>
<td>ligand centered</td>
</tr>
<tr>
<td>ISC</td>
<td>intersystem crossing</td>
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1 Introduction

The search for renewable energy sources as an alternative to fossil fuels is of high importance. To make efficient use of the freely available resource of solar energy by conversion of solar energy to electricity is important, both for environmental reasons and to be able to meet the increasing demand for electricity. Conventional solar cells, e.g. silicon based solar cells, are generally capable of stable and efficient solar energy conversion. However, a clear disadvantage is their production, which is both cost and energy expensive. Titanium dioxide (TiO$_2$) is an inexpensive and non-toxic material that is a photoactive semiconductor in crystalline form. Efficient usage of TiO$_2$ by itself in solar energy conversion devices is prevented by its wide band gap (3.2 eV) which corresponds to absorption of only a small fraction of the solar spectrum.

![Diagram of a dye-sensitized solar cell](image)

*Figure 1. Schematic pictures of (A) the basic parts, and (B) the photoinduced processes, of a dye-sensitized solar cell. Photoexcitation of the dye molecule adsorbed on the TiO$_2$ nanoparticle surface is followed by electron injection into the TiO$_2$ conduction band. The electron is transported through the nanoparticle network to the electrode, and further via the external load to the other electrode. The ground state of the dye is regenerated by an electron from the electrolyte, which in turn is regenerated at the electrode by electrons passed through the load.*
The optical activity of TiO2 can be increased substantially by adsorbing dye molecules on the semiconductor surface and thereby shifting the onset of its response to sunlight from the UV to the visible region. This is the basic idea behind dye-sensitized solar cells. These solar cells are based on porous films of nanocrystalline TiO2 particles that are covered by dye molecules (chromophores), and hence sensitize the semiconductor TiO2 towards sunlight. The nanoporous film offers a huge surface area for dye adsorption, which results in high light harvesting efficiency compared to the use of for example single crystals. The basic elements of a dye-sensitized solar cell as well as the electronic energy levels of the photoinduced processes are shown schematically in Figure 1. Following photoexcitation of the dye, the excited electron is transferred from the dye to the semiconductor conduction band, creating a charge separated state as the dye becomes oxidized. The electron is collected from the network of nanosized TiO2 particles at the electrode. An electrolyte, usually a I\(^{-}/I_3^-\) redox pair in solution, reduces the dye to its ground state and the redox pair is reduced at the other electrode, completing the electrical circuit in the cell.

![Figure 1](image)

Figure 1. Schematic illustration of the dye-sensitized TiO2 interface, where the chromophore is attached to the TiO2 surface via a spacer and an anchor group. Illumination results in the transfer of a photoexcited electron from the chromophore to the TiO2 nanoparticle across the spacer and anchor moieties.

Figure 2 shows a schematic example of a typical dye-TiO2 interface at the molecular level. The chromophore is chemically attached to the TiO2 nanoparticle by designated anchor groups. The chromophore and the nanoparticle surface can be separated by insertion of spacer groups between the chromophore and the anchor group in order to prevent charge recombination. Electron transfer across the dye-TiO2 interface is a very fast process, and can take place at a femtosecond time-scale when there is a strong geometrical and electronic coupling of the individual parts.

The most commonly used chromophores are ruthenium polypyridyl complexes. The wide-spread use of this class of complexes originates from their strong light absorption and excited states generated by the photoexcitation that are sufficiently long-lived for the complexes to initiate electron transfer.
to neighboring molecules prior to the onset of internal deactivation. Moreover, the possibilities to tune the properties of the chromophore through substitution and/or functionalization of the polypyrpyridyl ligands are many and varied. These complexes are also commonly used in so-called artificial photosynthetic devises, designed to produce hydrogen fuel (H₂) from water and sunlight.⁷

Quantum chemical calculations can provide information about geometrical and electronic structure at a detailed level. These calculations are both CPU and memory intensive and have therefore traditionally been limited to the study of relatively small model systems. However, the constant advances in theoretical methods, assisted by the advent of low cost high power computing resources have made it possible to study increasingly realistic model systems from first principles. In this thesis several aspects of the geometrical and electronic structures of dye-sensitized TiO₂ are treated with standard and time dependent density functional theory methods. One objective is to investigate the methodology necessary to describe large realistic model systems while maintaining high accuracy, so that the structure and electronic properties of dye-sensitized TiO₂ nanoparticle interfaces can be understood and predicted.

Chapter 2 provides an overview of the computational methods employed, and the results based on Papers I-VII are presented in Chapters 3-5. The roman numerals in the section and subsection headings in Chapters 3-5 refer to the paper(s) reporting the discussed results. A wide range of properties of ruthenium polypyrpyridyl dyes, e.g. geometrical, electronic and optical properties, as well as triplet excited states, are discussed in Chapter 3. The development of nanosized chemical models of anatase nanocrystals is presented in Chapter 4. In Chapter 5, dye and TiO₂ systems are combined to study the interfaces of these dye-sensitized systems. The thesis is concluded with some final remarks and a summary in Swedish.
2 Methods

2.1 Electronic structure theory

At the heart of quantum chemistry is the famous Schrödinger equation,

\[ \hat{H}_{\text{tot}} \psi_{\text{tot}} = E_{\text{tot}} \psi_{\text{tot}}, \]

here expressed in a time-independent non-relativistic form. \( \psi_{\text{tot}} \) is the total wave function which depends on the electronic and nuclear coordinates, \( E_{\text{tot}} \) is the total energy, and \( \hat{H}_{\text{tot}} \) is the Hamiltonian of the system, containing the kinetic and potential energy operators for all particles. In most quantum chemical calculations the Born-Oppenheimer approximation is invoked, which separates the motions of nuclei and electrons, so that an electronic Schrödinger equation for fixed nuclei is obtained,

\[ \hat{H}_{\text{elec}} \psi_{\text{elec}} = E_{\text{elec}} \psi_{\text{elec}}, \]

which only depends parametrically on the nuclear positions. Historically, most quantum chemical calculations have been based on the Hartree-Fock (HF) approximation to solve the electronic Schrödinger equation. In HF theory, each electron is described by a spin-specific one-electron function, a spin orbital constructed as a product of a spatial orbital and a spin function, and \( \psi_{\text{elec}} \) is expressed in the form of a single Slater determinant of spin orbitals. A set of one-electron equations known as the Hartree-Fock equations is obtained by minimizing the energy of the HF trial wave function based on the variational principle, which states that a trial wave function has an energy that is higher than or equal to the exact energy. These equations have to be solved iteratively until self-consistency using the self-consistent field (SCF) procedure, because the operators in these equations depend on the orbitals that one is seeking. In practical calculations, the Hartree-Fock orbitals can be defined as restricted, where electrons of different spin are, pairwise, described by a common spatial orbital, or as unrestricted where each electron has its own spatial distribution. The HF method generates solutions to the electronic Schrödinger equation, where the real electron-electron interaction is replaced by an average interaction. The consequence of this replacement is that the correlation of electrons’ motion is not described prop-
The correlation of electrons having the same spin is partially accounted for via an exchange interaction, but the correlation of electrons having opposite spins is not described. The exchange interaction is a non-classical interaction between two electrons with the same spin. A good description of electron correlation is important when calculating molecular properties. Hence, it is usually required to improve the HF description in order to obtain results that compare quantitatively, or even qualitatively, with experimental results. There are several approaches to systematically improve the HF approximation by including varying amounts of electron correlation, such as Møller-Plesset perturbation theory, configuration interaction, coupled-cluster theory, and multiconfiguration self-consistent field theory. For a detailed description of HF theory and electronic structure methods that go beyond this approximation, the reader is referred to the books of Szabo and Ostlund or Hehre, Radom, Schleyer and Pople.

2.2 Density functional theory

The main drawback with the HF based electronic structure methods that include electron correlation is that they become too time-consuming for most realistic molecular systems. This fact is the main motivation for using density functional theory (DFT) which has the inherent capability of treating electron correlation at a much lower computational cost. In DFT the basic variable, the wave-function, is replaced by the electron density, which is a function of only 3 spatial coordinates. The energy as well as other observables of the molecular system are obtained from by so-called functionals. As a consequence of the two theorems of Hohenberg and Kohn, the electron density may be considered the fundamental variable of multi-electron theory. In principle, knowing the electron density of the ground state, the ground state energy and all ground state molecular properties are possible to calculate. The second Hohenberg-Kohn theorem shows that the energy of the electron density obeys the variational principle in the sense that among all possible candidates of electron densities, the exact density is the one that also delivers the lowest energy. However, the Hohenberg-Kohn theorems do not provide the actual form of the energy functional $E[\rho]$, and to this date the functional form is still unknown.

The Kohn-Sham (KS) scheme is a computational strategy for approaching the true electron density and energy of an arbitrary atomic or molecular system. The KS method is the basis of the majority of DFT calculations performed today and has been employed in the present thesis. The idea behind the KS scheme was to make use of a hypothetical reference system composed of $N$ non-interacting electrons in $N$ orbitals, $\psi_i$, moving in an effective potential, $v_e$. For this type of system, a single Slater determinant describes the exact ground state wave function. The optimal orbitals for the
non-interacting system are obtained by solving the following one-electron equations

$$\left\{-\frac{1}{2} \nabla^2 + v_s\right\} \psi_i = e_i \psi_i ,$$  

(3)

with a Hamiltonian consisting of a kinetic energy term and an effective one-body potential. The total electron density is the sum of the orbital densities

$$\rho_i(\mathbf{r}) = \sum_i \left| \psi_i(\mathbf{r}) \right|^2 .$$  

(4)

The connection of the non-interacting electron system to a system of fully interacting electrons is established by choosing the effective one-body potential such that the electron distribution exactly equals the total ground state electron density of the real fully interacting system. Even though the actual form of the exact energy functional, \( E[\rho] \), is unknown, its ingredients can be expressed as


(5)

Here, \( \rho \) is the density of the fully interacting system, and the functional forms of the first three terms are known. The first term in equation 5 is the kinetic energy of a system composed of non-interacting electrons, the second term is the potential energy from Coulombic attraction between electrons and nuclei, and the third term is the classical electrostatic electron-electron repulsion energy. All contributions to the total energy not accounted for by the first three terms are collected in one term, \( E_{\text{xc}}[\rho] \), called the exchange-correlation functional. \( E_{\text{xc}}[\rho] \) formally includes all non-classical effects of exchange and correlation, but also the portion of the kinetic energy not covered by \( T_s[\rho] \). The exchange-correlation functional is also constructed to correct for the self-interaction error of \( J[\rho] \), which stems from the fact that the functional form of \( J[\rho] \) allows for an unphysical interaction of an electron with itself. Expanding the known functionals in equation 5 in terms of one-electron orbitals according to equation 4, results in

\[
E[\rho] = -\frac{1}{2} \sum_i \int \psi_i(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) + \sum_i \left( \sum_d \int \frac{Z_d}{|\mathbf{r}_i - \mathbf{r}_d|} \left| \psi_i(\mathbf{r}) \right|^2 \right) d\mathbf{r} \\
+ \frac{1}{2} \sum_i \sum_j \int \psi_i(\mathbf{r}) \left| \psi_j(\mathbf{r}) \right|^2 \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \left| \psi_j(\mathbf{r}) \right|^2 d\mathbf{r} d\mathbf{r'} + E_{\text{xc}}[\rho] .
\]

(6)

where \( M \) and \( N \) are the numbers of nuclei and electrons, respectively. Minimizing this energy with respect to independent variations in the orbitals (with orthonormality constraints), results in a set of one-electron equations, the KS equations,
\[ \hat{h}_{\text{KS}} \psi_i = \varepsilon_i \psi_i, \quad i = 1, 2, ..., N. \] (7)

The one-electron operator, \( \hat{h}_{\text{KS}} \), contains the kinetic energy, the potential due to the nuclei, the classical Coulomb potential and the potential generated by \( E_{xc}[\rho] \):

\[ \hat{h}_{\text{KS}} = -\frac{1}{2} \nabla^2 - \sum_j \frac{Z_j}{|R_j - \mathbf{r}|} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}) = -\frac{1}{2} \nabla^2 + v_{eff}(\mathbf{r}). \] (8)

The exchange-correlation potential, \( v_{xc} \), is defined as the functional derivative of the exchange-correlation energy with respect to \( \rho \),

\[ v_{xc}(\mathbf{r}) = \frac{\partial E_{xc}[\rho]}{\partial \rho(\mathbf{r})} \] (9)

Now, by comparing equation 3 with equation 7 and equation 8 it becomes clear that if the one-body potential, \( v_\iota \), in equation 3 is defined as \( v_{eff}(\mathbf{r}) \) in equation 8, the system with \( N \) non-interacting electrons is transformed to a system of fully interacting electrons. The KS equations are thus defined by setting \( v_\iota = v_{eff}(\mathbf{r}) \) in equation 3 and the orbitals obtained from these equations are termed KS orbitals. Since \( v_{eff}(\mathbf{r}) \) depends on the electron density, and hence on the KS orbitals, equation 7 has to be solved iteratively in a self-consistent manner, just as in HF theory. The energy of the system is then obtained by inserting the electron density constructed from the KS orbitals according to equation 4 into equation 5.

2.3 Exchange and correlation functionals

The explicit forms of the exact exchange-correlation functional and the exchange-correlation potential are not known. If they were, solving the KS equations would result in the exact ground state energy and DFT would be an exact theory. The quality of the density functional approach thus depends on the accuracy of the chosen approximation to \( E_{xc} \). The exchange-correlation functional is usually divided into two parts:

\[ E_{xc} = E_x + E_c, \] (10)

where \( E_x \) and \( E_c \) are functionals for the exchange part and for the correlation part of the energy, respectively. The exchange part contains only same-spin interactions while the correlation part contains both same-spin and opposite-spin interactions. The existing approximate exchange-correlation functionals can be subdivided according to how the electron density is treated in the calculation of the energy. In the simplest approximation, the local density approximation (LDA), the electron density is treated as an uniform electron gas, and \( E_{xc}^{\text{LDA}} \) is computed from
\[ E^{\text{LDA}}_{\text{xc}} [\rho] = \int \rho(\vec{r}) E_{\text{xc}}^{\text{LDA}} (\rho(\vec{r})) d\vec{r} \]  

where the integrand, \( E_{\text{xc}}^{\text{LDA}} \), is a functional depending only on the local density at a specific point, \( r \), in space. The exchange part of LDA is known as the \( \text{Xa} \) functional\(^{19} \) and the correlation part is called VWN\(^{20} \), and these functionals are most useful for systems where the real density is slowly-varying (i.e., for densities resembling a uniform electron gas), such as in large metal surfaces. In the generalized gradient approximation (GGA), which is the main approximation for all DFT methods used in this thesis, the exchange-correlation functional has the following general form

\[ E^{\text{GGA}}_{\text{xc}} [\rho] = \int f(\rho, \nabla \rho) d\vec{r} . \]  

In GGA functionals, the integrand is a functional depending not only on the local density, but also on the gradient of the electron density. These functionals are more useful than LDA functionals for calculations on molecules since such systems have regions where the density is far from slowly-varying. Another type of DFT methods includes a fraction of exact HF exchange energy (computed from the KS orbitals) in addition to exchange and correlation from pure DFT functionals. These methods are referred to as hybrid functionals, and have the general form

\[ E^{\text{Hybrid}}_{\text{xc}} = c E^{\text{HF}}_x + (1 - c) E^{\text{DFT}}_x + E^{\text{DFT}}_c , \]  

where \( c \) determines the amount of HF exchange included. In this thesis, the popular B3LYP hybrid functional\(^{21} \) has been used for most calculations. This functional includes 20% exact HF exchange and is expressed as:

\[ E^{\text{B3LYP}}_{\text{xc}} = (1 - a) E^{\text{LDA}}_x + a E^{\text{HF}}_x + b E^{\text{BLYP}}_x + c E^{\text{LYP}}_c + (1 - c) E^{\text{LDA}}_c . \]  

Here the components of the exchange part are LDA exchange \( (E^{\text{LDA}}_x) \),\(^{19} \) HF exchange \( (E^{\text{HF}}_x) \), and the GGA exchange functional Becke88 \( (E^{\text{BLYP}}_x) \).\(^{22} \) The correlation part of the B3LYP functional has contributions from LDA \( (E^{\text{LDA}}_c) \),\(^{20} \) and from GGA in the correlation functional of Lee, Yang, and Parr\(^{23} \) \( (E^{\text{LYP}}_c) \). The three parameters \( a, b, \) and \( c \) (0.20, 0.72 and 0.81, respectively) in equation 14 were determined by fitting to experimental data including atomization energies, ionization potentials, and electron affinities on a large set of molecules, using the correlation functional of Perdew and Wang\(^{24,25} \) instead of \( E^{\text{LDA}}_c \) and \( E^{\text{LYP}}_c \). In addition to B3LYP, four other exchange-correlation functionals have been employed in this thesis. These are the PBE1PBE hybrid functional\(^{26} \) which incorporates 25% exact HF exchange, the pure BLYP\(^{22,23} \) and HCTH\(^{27} \) GGA functionals and a pure GGA functional composed of exchange from PW86\(^{25} \) and correlation from PW91\(^{31} \), a combination which in the following is referred to as PW.
For a detailed description of DFT, the reader is referred to the book of Parr and Yang.\textsuperscript{29} In addition, the book of Koch and Holthausen\textsuperscript{30} can be recommended for chemists interested in doing practical DFT calculations.

2.4 Basis sets

The individual orbitals $\psi_i$, molecular or atomic depending on the investigated system, are expanded in terms of a set of basis functions $\{\varphi_i\}$, centered on the nucleus or nuclei,

$$\psi_i = \sum \!_{\nu} c_{i\nu} \varphi_{\nu},$$

where the orbital expansion coefficients, $c_{i\nu}$, are optimized during the calculation. The set of basis functions available for an expansion is called the basis set. These basis functions can be Slater type orbital (STO) functions which are similar to the orbitals obtained by the analytical solution of the Schrödinger equation for the hydrogen atom. However, a more efficient computation of two-electron integrals is achieved with Gaussian type orbital (GTO) functions. It is therefore more common to use so-called contracted Gaussian functions, in which several primitive GTO functions are combined in a fixed, predefined linear combination.

The smallest possible basis set representation is termed a minimal or single zeta basis set and comprises only the number of functions required to accommodate all the electrons of the atoms of the system. Doubling the number of functions, a double zeta basis set, provides a more flexible description since there are two sets of functions for each occupied shell of the atoms. So-called split-valence basis sets, where the description is split into an inner component describing the core electrons with one level of representation, e.g. minimal basis, and an outer component describing the valence electrons with another level of representations, e.g. a double zeta basis. This splitting is motivated by the fact that chemistry is mainly dependent on the valence electrons, and core electrons have little influence on chemical processes. Additional improvements of the basis set can be achieved by adding polarization functions and/or diffuse functions.\textsuperscript{31} In this thesis, the majority of calculations were performed using either Dunning’s D95V basis set\textsuperscript{32} or the Pople family of basis sets.\textsuperscript{16,33}

The choice of basis set is very important for the quality of the computational results. A sufficiently flexible and well-balanced basis set must be used to obtain accurate results, but accuracy and computational cost has to be weighted against each other. This trade-off becomes increasingly important to consider when large systems are investigated, which is the case in this thesis.
2.5 Frozen core approximation and effective core potentials

The size of the computational problem can be reduced by reducing the size of the variational part of the basis set and hence more efficient computations can be achieved. Two such approaches are the frozen core approximation and the use of effective core potentials (ECPs). Both are based on the philosophy that it is less important to have a very accurate and highly flexible description of the core electrons than the chemically more important valence electrons, as already mentioned above. A frozen core calculation is in essence an all-electron calculation which ignores the slight change in the atomic core orbitals upon formation of the chemical bond. The expansion coefficients of the frozen core orbitals are kept fixed at predetermined values during the calculation. Note that the words valence and core used here are not the traditional chemist’s valence and core systems. The frozen core approximation is used in the basis sets employed by the ADF program (used in Papers V and VI), which uses Slater type basis sets in which the orbitals of the core of a given atom has been predetermined by high level calculations with small, medium or large frozen core.34 The exact definition of the frozen core orbitals used with a basis set is stored in the corresponding database file in terms of expansion coefficients. In the ECP approach, on the other hand, the core electrons are replaced by analytical functions that reasonably accurately, and very efficiently, represent the combined nuclear-electronic core to the remaining electrons. That is, the remaining valence electrons are treated explicitly in a potential of fixed atomic ions consisting of the nucleus and the core electrons. The ECPs are fixed and transferable one-electron operators that are determined from experiments or high level computational data. The potential is different for each angular momentum. ECPs can also vary in how many electrons they replace, from small- to large-core ECPs. Moreover, while all-electron relativistic calculations are very expensive, using ECPs that take part of the relativistic effects into account is an economical way to include certain relativistic effects.

There are many available ECPs with different parameters. In this thesis two main ECP families are used: the commonly used ECPs of Hay and Wadt and associated double zeta basis sets (LANL2DZ),32,35 and the less known large-core ECPs of Durand and Barthelat and associated double zeta basis sets by Boutellier which we refer to as VDZ36. For the VDZ ECP/basis sets, an extra \(d\)-polarization function has been added to the basis set for the phosphorous atom in order to improve its description.37 In addition, when an additional \(sp\) shell is added to the oxygen atom basis set,38 the ECP/basis set combination is referred to as VD(T)Z. The Hay-Wadt and Durand-Barthelat ECPs are all non-empirical ECPs that have been obtained by fitting to a high quality all-electron wave function for each particular atom. Two advantages of these ECP/basis set combinations for the applications in this thesis are
that LANL2DZ describes ruthenium with inclusion of relativistic effects and VDZ is highly efficient for titanium. In addition to these ECPs, some calculations have been performed with the Stuttgart-Dresden (SDD) ECPs,\textsuperscript{39} and with CEP-31 and CEP-121\textsuperscript{40}.

By using either the frozen core approximation or ECPs, computational saving can be achieved with reasonably little loss of information concerning the investigated physical and chemical properties.

2.6 Absorption spectra using time-dependent density functional theory

Time-dependent density functional theory (TD-DFT) is an extension of DFT to time dependent problems, such as a molecular system’s interaction with a time-dependent external field.\textsuperscript{41} In the case of a spectroscopic measurement of an optical absorption spectrum the external field is an electromagnetic wave. Under these conditions, the effect on the system by the external field is sufficiently small to allow that the system’s response is described by time-dependent perturbation theory. Within this approach, the excitations are expressed in terms of ground state properties and excited states are not evaluated explicitly.

The simplest form of the interaction of the system and the electromagnetic wave is the electric dipolar interaction, giving the time dependent perturbation needed to be considered, for example, the following form:

\[
H^{(1)}(t) = -\tilde{\mu} \cdot \vec{E}(t),
\]  

where \(\tilde{\mu}\) is the dipole moment operator of the electrons, and the electric field \(\vec{E}\) is oscillating with frequency \(\omega\) in the simple case of monochromatic light. The linear response of the system to such a perturbation is described by the dynamic polarizability \(\alpha(\omega)\). Since the molecules are randomly oriented in for example solution and gas phase, the interesting quantity for comparisons with experiments is the mean dynamic polarizability, \(\overline{\alpha}(\omega)\), a property that has the following form:

\[
\overline{\alpha}(\omega) = \sum_{\text{excited states}} \frac{f_i}{\omega_i - \omega^2};
\]

where \(\omega_i = E_i - E_0\) are the excitation energies and \(f_i\) are the oscillator strengths, which contain the transition dipole moments

\[
f_i = \frac{1}{2} \langle E_i - E_0 \rangle \langle \Psi_0 | \tilde{\mu} | \Psi_i \rangle^2.
\]

The dynamic polarizability has poles (diverges) at frequencies corresponding to excitation energies. Hence, the absorption spectrum of a system
can in principle be obtained as the poles and residues (numerator at the poles) of the mean dynamic polarizability.\textsuperscript{42}

It appears to be generally accepted that TD-DFT provides fairly accurate excitation energies as long as low-energy transitions involving valence states are investigated.\textsuperscript{30} Hybrid functionals, such as B3LYP, seem to yield slightly more accurate results than simple GGA functionals especially for charge-transfer states.\textsuperscript{43}

2.7 Polarizable continuum solvent model

In a polarizable continuum model (PCM), the molecule is surrounded by a dielectric medium, the polarizable continuum, with a given dielectric constant, $\varepsilon$. This medium is polarized in response to the charge distribution (nuclei and electrons) that it experiences and produces an electric field, called a reaction field, which in turn polarizes the molecule. The resulting slightly changed charge distribution alters the reaction field somewhat, which again leads to further polarization of the molecule. This process continues until equilibrium is reached. In the PCM implemented in the Gaussian program, the reaction field is represented through charges located on the surface of the molecular cavity.\textsuperscript{44} The molecular cavity can be created in several ways, but is generally based on interlocking van der Waals-spheres centered at atomic positions. The surface of this cavity is smoothed (for numerical reasons) and in the PCM model approximated by many small planar surface elements (tesserae) of given area. Charges are then placed on each of the surface elements to represent the reaction field of the dielectric medium.

The extent to which the medium can be polarized and hence the ultimate strength of the reaction field is controlled by the magnitude of the dielectric constant. In this work, PCM models of acetonitrile ($\varepsilon \approx 37$) ethanol ($\varepsilon \approx 25$) and benzene ($\varepsilon \approx 2$) were used. For comparison it can be mentioned that water is usually modeled using a dielectric constant of ca. 80.
3 Ruthenium polypyriddy dyes

Central to the function of a dye-sensitized semiconductor system or to an artificial photosynthetic device is the properties of the chromophore. The role of the chromophore is to absorb solar energy in the form of visible light and convert it to excitation energy that through electron transfer leads to a charge separated state. Ruthenium polypyriddy complexes have been used extensively as chromophores in devices for solar energy conversion, as well as for the study of light-induced charge separation in general.45,46

Figure 3. A schematic energy level diagram illustrating key steps in the photoinduced processes, and the chemical structure of Ru^{II}(bpy)_3.

The model of the photoinduced processes in Ru(II) polypyriddy complexes is mainly based on the knowledge about the well-studied Ru^{II}(bpy)_3 (bpy = 2,2’-bipyridine) complex.45-49 Figure 3 shows a schematic energy level diagram that describes the main photophysical steps. The absorption of visible light, with an absorption maximum around 450 nm, results in metal-to-ligand charge transfer (MLCT) excitations from the ground (S_0) state to singlet MLCT (1MLCT) states. Absorption is followed by rapid and efficient decay of the 1MLCT states via intersystem crossing (ISC) to the lowest-lying MLCT triplet (3MLCT) excited states, which are the states responsible for observed luminescence. The lifetime of the 3MLCT states are crucial to the photochemical activity in artificial photosynthetic systems, since it has to be sufficiently long to allow for the relevant electron transfer reactions to occur, i.e. formation of a charge separated state, prior to decay back to the ground
state. Note however that the 3MLCT lifetime may be less important for ultrafast electron injection into TiO₂ in dye-sensitized semiconductor systems.

The popularity of Ru II(bpy)₃ is mainly due to its long-lived excited 3MLCT states of ~1μs at room temperature.⁴⁵ Besides radiative (emission) and non-radiative decay directly from the 3MLCT states back to S₀, a third major deactivation pathway of the 3MLCT states is thermal population of short-lived metal centered triplet (3MC) states which is followed by non-radiative decay to S₀ or photochemical reactions e.g., ligand dissociation.⁴⁸,⁵⁰

The energy diagram in Figure 3 has been simplified to involve only two states of the singlet and triplet state manifolds, respectively, which will be the basis of the following discussion.

3.1 Geometrical and electronic structure

In the ground state electronic structure of the free ruthenium atom the highest occupied orbitals correspond to five degenerate 4d orbitals (dₓᵧ, dᵧz, dₓz, dₓ²−y², and dₑ). In Ru(II) polypyridyl complexes, however, the presence of the ligands induces an energetic splitting of these 4d-orbitals, which results in a separation into a set of occupied t₂g orbitals (dₓᵧ, dᵧz, dₓz) and a set of unoccupied eₐ orbitals (dₑ). The geometrical and electronic structure of RuII(bpy)₃ has been calculated with various quantum chemical methods.⁵¹–⁵⁵

Figure 4 shows the molecular orbital diagram calculated for Ru II(bpy)₃ at the B3LYP/LANL2DZ level, with the five ruthenium 4d-type molecular orbitals (MOs) shown on the right. The main orbital character of the lowest unoccupied MO (LUMO) in RuII(bpy)₃ is ligand bpy-ʌ.*

A simple orbital description can be used to describe the photoinduced processes discussed above in terms of perturbations of the ground state electronic structure. Photoexcitation (absorption) transfers one of the Ru 4d-electrons (t₂g) to the LUMO that has orbital character primarily on the ligands, i.e., a metal-to-ligand charge transfer (1MLCT) state. The 3MLCT state corresponds to the MO arrangement obtained when changing the two unpaired electrons from opposite spin in the 1MLCT state to same spin in the 3MLCT state. The 3MC state results from further promotion of the electron which was initially excited to the LUMO to one of the unoccupied dₑ orbitals.

The relatively long excited state lifetime of Ru II(bpy)₃ is thought to be related to a strong ligand field arising from its nearly perfect octahedral ligand coordination to the central ruthenium ion. The nature of the bpy ligands and their spatial orientation in three directions around the RuII core (D₃ symmetry-
try) result in a large ligand field splitting. A strong ligand field is thought to give rise to a large relative energy between $^3$MLCT and $^3$MC states and a large thermal activation barrier for the $^3$MLCT to $^3$MC conversion. Hence, the ligand field splitting is believed to be important for the excited state lifetime.\(^{46}\)

Figure 4. Calculated (B3LYP/LANL2DZ) molecular orbital diagram of Ru$^{	ext{II}}$(bpy)$_3$, with the LUMO and the five Ru 4d-orbitals shown on the right. The arrows indicate the ligand field splitting, $\Delta_0$, and the HOMO-LUMO gap. HOMO = highest occupied molecular orbital and LUMO = lowest unoccupied molecular orbital.

As mentioned, the spatial orientation (good coordination at short distance) is presumably responsible for the long excited state lifetime of Ru$^{	ext{II}}$(bpy)$_3$. However, the spatial orientation of the ligands is also one of the disadvantages of Ru$^{	ext{II}}$(bpy)$_3$. In many applications, the possibility for formation of quasi-linear donor-chromophore-acceptor systems is highly desirable in order to be able to control the spatial separation of the donor and acceptor parts and to control the direction of electron transfer. Functionalization of Ru$^{	ext{II}}$(bpy)$_3$ leads to several possible isomers, where the majority of isomers do not form linear arrangements that can provide a vectorial transfer direction. In this respect, complexes based on the 2,2':6',2"-terpyridine (tpy) ligand (see Figure 5) are attractive alternatives because they offer the possibility of forming linear dye complex structures via functionalization at the 4'-position of the central pyridyl in each tpy ligand. Moreover, the tpy ligand coordinates with all three nitrogens to the metal, \textit{i.e.} tpy is a tri-dentate ligand, which leads to a complex that is stable towards ligand loss due to the chelate effect.\(^{56}\) However, the excited state lifetime for Ru$^{	ext{II}}$(tpy)$_2$, \(\sim 250\) ps,\(^{57}\) is much shorter than for Ru$^{	ext{II}}$(bpy)$_3$, \(\sim 1\) \(\mu\)s,\(^{46}\), which is believed to be caused by the rigidity of the tpy ligand that leads to a less octahedral ligand coordination and thus a weak ligand field.
The photophysical and photochemical properties of Ru(II) polypyridyl complexes can be altered through substitution and/or functionalization of the ligands to achieve maximum efficiency for various applications. By the design of new Ru(II) polypyridyl complexes improvements in e.g. absorption, excited state lifetime or certain structural properties can be achieved. The properties of the excited states ultimately depend on the ligands bonded to the Ru(II) ion.

One design strategy to prolong the 3MLCT excited state lifetime of Ru(II)(tpy)2-like complexes is to make structural modifications of the tpy ligand in order to increase the flexibility of the ligand so that a more octahedral metal coordination can be achieved.58 In that way, the advantageous structural properties of Ru(II)(tpy)2 can be maintained while the ligand field strength is increased (ligand field splitting increased) and thus the probability for deactivation via MC states is reduced.

3.1.1 Octahedral coordination and ligand field splitting (I)

![Diagram of Ru(II) polypyridyl complexes]

*Figure 5. Ru(II) polypyridyl complexes: Ru(II)(py)6, cis-, or trans- Ru(II)(bpy)2(py)2, Ru(II)(tpy)2, Ru(II)(bmp)2, Ru(II)(bm3p)2, and Ru(II)(pmp)2. The axial pyridyls are indicated by N2 and N5.*

The connection between coordination geometry, ligand field splitting (indication of the difference in relative stability of the 3MC state) and excited state lifetime was investigated by studying the geometrical and electronic structure of Ru(II)(bpy)3, Ru(II)(tpy)2 and six other Ru(II) polypyridyl complexes (shown in Figure 5) with a common basic structure; one Ru(II) ion and six
pyridyls, where the pyridyls are connected in various ways. For five of these eight complexes, the experimental excited state lifetime is available. The singlet ground state geometries were fully optimized at the B3LYP/LANL2DZ level of theory. An octahedricity measure, the root-mean-square (RMS) angle deviation, based on the fifteen N-Ru-N angles was introduced to be able to determine how much the structure of a particular complex deviates from ideal N-Ru-N angles (180° and 90°). This octahedricity measure ranges from 0.5-3.0° and clusters Ru^{II}(bpy)$_3$, cis-Ru^{II}(bpy)$_2$(py)$_2$, Ru^{II}(py)$_6$, Ru^{II}(pmp)$_2$ and Ru^{II}(bpm)$_2$ as close to octahedral, and Ru^{II}(tpy)$_2$, Ru^{II}(bm3p)$_2$, and trans-Ru^{II}(bpy)$_2$(py)$_2$ as somewhat less octahedral. The ligand field splitting $\Delta_O$, i.e. the energy difference between the highest occupied $t_{2g}$ orbital and the lowest unoccupied $e_g$ orbital, was extracted directly from the electronic structure.

The ligand field splitting ranges from 5.6-6.0 eV for these complexes within the given method. A plot of the octahedricity vs. this orbital energy difference is shown in Figure 6 (left). A relationship between how octahedral the structure is and the size of the ligand field splitting can be made out for similar ligands, such as for example pmp, bpm and bm3p. However, the size of $\Delta_O$ is not only dependent on how octahedral the ligand coordination is (angular dependence), but also on the distance between the ligand and the ruthenium core (radial dependence). For example, Ru^{II}(py)$_6$ has a highly octahedral coordination with an RMS angle deviation of 0.5° but a relatively small $\Delta_O$ of 5.60 eV, which is similar to that of the obviously less octahedral Ru^{II}(tpy)$_2$, due to the long Ru-N bonds, 2.20 Å (axial pyridyls) and 2.17 Å (equatorial pyridyls), in the optimized ground state geometry.
3.1.2 Ligand field splitting and excited state lifetime (I)

The calculations indicate an apparent correlation between $\Delta_0$ and the experimental excited state lifetime, such that a small increase in $\Delta_0$ over 6 eV appear to result in a large increase in excited state lifetime, see Figure 6 (right). However, a more extensive study, extending the limited data set used in this study, is necessary to firmly confirm a relationship and establish the character of it. Such a correlation requires that the energy of the $^3$MLCT is very similar for all the compared complexes. This may not generally be the case for all Ru(II) polypyridyl complexes as will be seen later for RuII(pmp)$_2$.

3.2 Triplet MLCT and MC states

Manipulation of the energy difference between the $^3$MLCT and $^3$MC states of RuII(tpy)$_2$-like complexes in order to prolong excited state lifetimes by minimizing thermal population of $^3$MC states is attempted by various design strategies. Besides modifying the flexibility of the tpy ligand discussed above, some other examples are to design ligands with electron- withdrawing or $\pi$-donating substituents, ligands with extended $\pi$ systems, and strong $\sigma$-donor ligands. Which ever strategy is chosen, it is always important to know and understand the effect of the various modifications. Standard DFT offers the possibility to locate the actual structures and relative energies of the lowest $S_0$, $^3$MLCT and $^3$MC states. Although the calculation of these states is in principle straightforward, the number of calculated $^3$MC states found in the literature is surprisingly few. Instead the most common approach is to estimate the energy difference between the $^3$MLCT and $^3$MC states by TD-DFT calculations of vertical triplet excitations from the ground state.

3.2.1 RuII(bmp)$_2$ and RuII(bm3p)$_2$ (II)

By insertion of a methylene group between two of the pyridyls in tpy, a non-planar bpy-py like ligand with a single carbon-link connecting the two moieties is formed (see Figure 5). This ligand, referred to as bmp, forms upon meridional coordination a trans relationship of the middle pyridyls of the two ligands, that can be functionalized to form quasi-linear complexes. Both X-ray crystal and computational data for RuIII(bmp)$_2$ show a more octahedral environment around Ru than in RuII(tpy)$_2$, and the excited state lifetime was improved to 15 ns. With the anticipation that an even more increased lifetime could be obtained by restricting the motion of the lone pyridyls, thus preventing the pyridyl from loosing coordination to the metal, the methylene hydrogens in the bmp ligand were substituted with methyl groups (iso-
propylene bridge) forming the bm3p ligand (see Figure 5). However, instead of increasing the excited state lifetime, it was severely reduced to 0.3 ns for Ru\textsuperscript{II}(bm3p)\textsubscript{2}, which is similar to that of Ru\textsuperscript{II}(tpy)\textsubscript{2}. Both the X-ray crystal structure and DFT calculations show that the geometry of the Ru\textsuperscript{II}(bmp)\textsubscript{2} complex is more octahedral than the Ru\textsuperscript{II}(bm3p)\textsubscript{2} complex, where the RMS angle deviations are 1.9° and 2.3°, respectively. The largest structural difference is seen for the orientation of the lone pyridyls, where the N-Ru-N angles between the isolated pyridines is 108.64° in Ru\textsuperscript{II}(bm3p)\textsubscript{2}, and only 98.9° in the structure of Ru\textsuperscript{II}(bmp)\textsubscript{2}. The calculated ligand field splitting (\(\Delta_0\)) indicates a slightly more favorable triplet surface for Ru\textsuperscript{II}(bmp)\textsubscript{2}, however, the difference is small, only 0.10 eV at the B3LYP/LANL2DZ level.

In the geometry optimizations of the three states of Ru\textsuperscript{II}(bmp)\textsubscript{2} and Ru\textsuperscript{II}(bm3p)\textsubscript{2}, the geometric distortions from the S\textsubscript{0} to the 3MLCT state result in slightly shorter Ru-N bonds, and from S\textsubscript{0} to the 3MC state in clear elongation of the equatorial Ru-N bonds (xy-plane) of 0.09-0.24 Å which corresponds to population of the \(d_{x^2-y^2}\) orbital. The calculated spin density of the optimized triplet states characterizes the two states as having ca. one odd spin at the Ru center and the remaining distributed primarily over the bpy moieties in the 3MLCT state and ca. two net spin at the Ru core in the 3MC state for both Ru\textsuperscript{II}(bmp)\textsubscript{2} and Ru\textsuperscript{II}(bm3p)\textsubscript{2}.

![Figure 7](image.png)

**Figure 7.** Calculated energy diagrams of Ru\textsuperscript{II}(bmp)\textsubscript{2} and Ru\textsuperscript{II}(bm3p)\textsubscript{2} (left) and Ru\textsuperscript{II}(py)\textsubscript{6} and Ru\textsuperscript{II}(pmp)\textsubscript{2} (right). The nuclear coordinate is defined as the sum of Ru-N distance displacements relative to the ground state geometry.

The potential energy diagrams for the two complexes are shown in Figure 7 (left), Ru\textsuperscript{II}(bmp)\textsubscript{2} in grey and Ru\textsuperscript{II}(bm3p)\textsubscript{2} in black. The nuclear coordinate is defined as the sum of Ru-N distance displacements relative to the ground state geometry. The energies used to construct the diagrams are the total electronic energy of optimized states (crosses), vertical single-point energies of the S\textsubscript{0} surface for the 3MLCT and 3MC geometries (dots) and vertical
singlet and triplet excitation energies of the $S_0$ state (horizontal bars, SX and TX). The slope of the $^3$MC surface is estimated by the lowest vertical triplet excitation of significant MC character. The diagrams confirm the indications of a less favorable potential energy surface for Ru$^{II}$(bm3p)$_2$ compared to Ru$^{II}$(bmp)$_2$. The reaction energy for $^3$MLCT to $^3$MC conversion is $0.05 \text{ eV}$ for Ru$^{II}$(bmp)$_2$ and $-0.06 \text{ eV}$ for Ru$^{II}$(bm3p)$_2$, i.e. the $^3$MC state of Ru$^{II}$(bm3p)$_2$ is more stable than the $^3$MLCT state. In addition, the vertical distance between the $^3$MLCT and $^3$MC surfaces from $S_0$, $T_1$ and $T_7$ in Figure 7, is $0.15 \text{ eV}$ larger for Ru$^{II}$(bmp)$_2$. Moreover, a rough estimate of the difference in activation barrier for the $^3$MLCT to $^3$MC conversion between Ru$^{II}$(bm3p)$_2$ and Ru$^{II}$(bmp)$_2$ obtained by a simple Marcus equation$^{64}$ is ca. $0.06 \text{ eV}$ higher in the latter case. In summary, the less favorable relative potential energies in terms of photophysical properties for Ru$^{II}$(bm3p)$_2$ could explain the observed difference in excited state lifetime.

3.2.2 Ru$^{II}$(pmp)$_2$ and Ru$^{II}$(py)$_6$ (I)

Along the same line of design strategy as for the bmp ligand (increased flexibility to give more octahedral coordination), even more flexibility for perfect metal ion coordination could be offered by insertion of yet another methylene into the bmp ligand between the two pyridyls of the bpy moiety, giving a 2,6-dipicolylpyridine ligand (pmp), see Figure 5. No literature data is available for the resulting homoleptic Ru(II) complex, Ru$^{II}$(pmp)$_2$, but calculations can potentially predict its properties. The Ru$^{II}$(pmp)$_2$ complex is expected to have similar electronic properties as Ru$^{II}$(py)$_6$ but have an additional stability due to the two tri-dentate ligands instead of six mono-dentate ligands (chelate effect$^{56}$). Ru$^{II}$(py)$_6$ is known to be sensitive to ligand substitution$^{50,65}$, and hence limited data for this complex exist.

The pmp ligands coordinate in a meridional fashion to form a wave-like ligand structure such that the bends of the methylenes are pointing in opposite directions within a ligand. The additional flexibility offered by the two methylene groups in pmp creates a highly octahedral complex that has relative pyridyl orientations highly similar to that in Ru$^{II}$(py)$_6$. The calculated RMS angle deviations for Ru$^{II}$(pmp)$_2$ is $0.9^\circ$ to be compared to $0.5^\circ$ for Ru$^{II}$(py)$_6$. The Ru-N distances are shorter in Ru$^{II}$(pmp)$_2$, and the calculated Ru-N distances in the two complexes indicate that the lowest unoccupied d-orbital is $d_{x^2-y^2}$ for Ru$^{II}$(pmp)$_2$ since the equatorial Ru-N distances are longer than the axial, and that the $d_{z^2}$ orbital is the lowest in Ru$^{II}$(py)$_6$ since the axial Ru-N distances are longer in this case. This is confirmed by the electronic structure, which also shows a larger ligand field splitting in Ru$^{II}$(pmp)$_2$ than in both Ru$^{II}$(bmp)$_2$ and Ru$^{II}$(py)$_6$, due to better octahedral coordination than in Ru$^{II}$(bmp)$_2$ and shorter Ru-N distances than in Ru$^{II}$(py)$_6$. The simulated absorption spectrum of Ru$^{II}$(pmp)$_2$ is highly similar to that of Ru$^{II}$(py)$_6$, which indicates that Ru$^{II}$(pmp)$_2$ does not absorb visible light. The lack of
visible absorption can be explained by the large HOMO-LUMO gaps relative to that of e.g. Ru$^{II}$(bpy)$_3$ and Ru$^{II}$(tpy)$_2$. In bpy and tpy, a bonding MO contribution over the C2-C2' connection between the pyridyl rings stabilizes the LUMO level and thus decreases the HOMO-LUMO gap which in turn facilitates low energy excitations. Since Ru$^{II}$(pmp)$_2$ and Ru$^{II}$(py)$_6$ lack this type of LUMO stabilization, they also lack the low energy excitations that fall into the visible spectrum.

Geometry optimization of the 3MLCT state of Ru$^{II}$(pmp)$_2$ results in a structure that again has slightly shorter Ru-N distances than S$_0$, and with half of the net spin at the ruthenium core and half on the ligands, primarily on the axial pyridyls. In the optimized 3MC state, with a net spin close to two at the Ru centre, the Ru-N distances in the equatorial plane have been symmetrically elongated ca. 0.20 Å relative to the S$_0$ geometry, hence indicating population of the Ru 4d$_{x^2-y^2}$-type orbital. However, the calculated energy diagram in Figure 7 (right, black diagram) shows unfavorable energetics for the Ru$^{II}$(pmp)$_2$ system. Firstly, the 3MC state is 0.6 eV more stable than the 3MLCT state. Secondly, the difference in the lowest vertical 3MLCT and 3MC type excitations from S$_0$, i.e. the difference between T5 and T1 in Figure 7, is only 0.16 eV. Hence, the diagram indicates a very low barrier for 3MLCT to 3MC conversion. Although the calculations predict Ru$^{II}$(pmp)$_2$ to have advantageous structural properties, the calculated energetic properties, both in terms of absorption and relative stability of important states, suggest that Ru$^{II}$(pmp)$_2$ cannot be used as a photosensitizer. The electronic structure of the pmp ligand could possibly be modified for instance by a substitution at the pmp ligand that will lower the LUMO level in energy, to enable absorption of visible light and reverse the energetic order of the 3MLCT and 3MC states.

All attempts to locate a 3MLCT state of Ru$^{II}$(py)$_6$ failed. Calculation of the lowest vertical singlet and triplet excitation from S$_0$ reveals excitations of MC character. Therefore, instead of locating a 3MLCT state geometry, the triplet geometry optimization from the optimized S$_0$ geometry, automatically results in a 3MC state with significantly elongated axial Ru-N bonds. The calculated energy diagram of Ru$^{II}$(py)$_6$ shown in Figure 7 explains the photochemical instability towards ligand loss. Hence, according to the calculations, connecting the pyridine rings by methylene groups prevents dissociation of the ligands, so that the excited state manifold of Ru$^{II}$(pmp)$_2$ consist of a stable 3MLCT state in contrast to Ru$^{II}$(py)$_6$. 


3.3 Anchor and spacer group functionalization and effects of surrounding environment

Using Ru(II) polypyridyl complexes as photosensitizers in dye-sensitized metal oxide systems requires functionalization with designated anchor groups, such as carboxylic or phosphonic acid groups, that binds the chromophore to the metal oxide surface. Spacer groups can be introduced between the chromophore and the anchor group in order to spatially separate the chromophore and the semiconductor. By the use of rigid rod-like spacers, both the distance between and the relative orientation of the chromophore and the surface can be controlled. Rigid spacer groups are used in a similar way in donor-acceptor dyads for artificial photosynthetic applications to optimally separate the individual parts. In dye-sensitized solar cell applications, the spacer optimally provides structural control such that the dye stands perpendicular to the surface, mediates electron transfer and prevents charge recombination.

3.3.1 Ru(II)(bpy)₃ functionalized with OPE rigid rods (III)

Figure 8. Rigid rod linker parts: ethynylene (E), p-phenylene (Ph), bicyclo[2.2.2]octylene (Bco) and isophtalic acid (Ipa).

Oligophenyleneethynylene (OPE) groups can be used as spacers. Due to the structure of the connected ethynylene (E) and p-phenylene (Ph) moieties a highly rigid structure can be obtained, which can be extended to very long rigid rod linkers. To maintain the rod-like structure upon attachment to a surface, an isophtalic acid (Ipa) group with two carboxylic acid anchor groups can be attached to the chromophore-rigid-rod. Studies have shown that the functionalization of Ru(II)(bpy)₃ by OPE rods alter the absorption spectra, and that different OPE rods have slightly different effects. The absorption spectrum of Ru(II)(bpy)₃ consists of two main absorption bands, a MLCT band in the visible region with absorption maximum at ~450 nm, involving excitation from the highest occupied Ru 4d orbitals to the lowest unoccupied bpy-π* molecular orbitals, and a band at ~290 nm involving bpy ligand centered (LC) π→π* excitations. However, when comparing the experimental absorption spectrum in acetonitrile solution of Ru(II)(bpy)₃ with those of Ru(II)(bpy)₃-E-Ipa, Ru(II)(bpy)₃-E-Ph-Ipa, and Ru(II)(bpy)₃-E-Bco-E-Ipa (Bco = bicyclo[2.2.2]octylene, the various structural elements are shown
in Figure 8), the MLCT absorption maximum is red-shifted and additional features between the MLCT and LC bands appear for RuII(bpy)3-E-Ipa (at ~325 nm) and RuII(bpy)3-E-Ph-E-Ipa (at ~350 nm).

In order to investigate the influence of the rigid rods on the electronic and spectral properties of the parent chromophore, the absorption spectra for RuII(bpy)3 and the three derivatives were simulated by TD-B3LYP/LANL2DZ with standard PCM acetonitrile solvent. In general, the features of the experimental spectra are well reproduced by the simulations. The calculations show that functionalization of RuII(bpy)3 red-shifts both the absorption threshold and the MLCT absorption maximum, especially with the E-Ipa and E-Ph-E-Ipa rigid rod linkers. This effect can be explained by a delocalization of the bpy-π* character in the LUMO onto the rigid rod, which lowers the energy of the LUMO. In all three complexes the orbital character of the LUMO is extended to the adjacent ethynylene, and for E-Ipa and E-Ph-E-Ipa rods also to the subsequent phenyl moiety (see Figure 9). However, the saturated Bco unit breaks the π-conjugation and thus has a spectrum more similar to that of the parent complex. Moreover, the new features in the 300-400 nm region are assigned by the calculations to π→π* excitations on the rigid rod.

For RuII(bpy)3, the gas phase and PCM acetonitrile spectra are highly similar and reproduce the experimental features well. However for the E-Ph-E-Ipa and E-Bco-E-Ipa containing dyes, the calculated gas phase spectra contain low-energy excitations such that the absorption thresholds are around 800 and 1000 nm, respectively. These features are not present in the experimental spectra. When the spectrum of RuII(bpy)3-E-Ph-E-Ipa is obtained using the PCM solvent model with various standard solvents (hexane, ethanol and acetonitrile) the low-energy excitations are essentially absent. The inclusion of two PF6 counter ions in the model has the same effect. An explanation for this effect of the surroundings is found in changes in the spatial

![Figure 9. HOMO and LUMO of RuII(bpy)3 dyes containing rigid rods in PCM acetonitrile solvent and gas phase.](image)
distribution of certain orbitals and the relative energetic ordering of the calculated molecular orbitals in the different environments. As illustrated in Figure 9 by the LUMO and HOMO calculated in PCM acetonitrile solvent model and in gas phase, the inclusion of chemical environment can change the predicted optical behaviour of the system. In the gas phase, the HOMO is located on the rod and the LUMO is located on the unsubstituted bpy ligands. Excitations of HOMO→LUMO character will take an electron from the rod and populate an orbital localized on the Ru II(bpy)3 chromophore. These are low energy excitations that reduce the chromophore, rather than oxidize it.

In the acetonitrile solvent model, the HOMO is instead located mainly on the Ru(II) ion, and the LUMO is located on the substituted bpy ligand, with orbital contribution also on the rod. These changes in orbital character make the peaks with long wavelengths in the gas phase spectrum disappear and reverse the direction of excitations of HOMO→LUMO character compared with gas phase results. It appears that both a solvent model and explicit counter ions screen the positive Ru(II) ion in such a way as to remove the spurious long wavelength excitations seen for the bare functionalized dye.

Investigation of the 3MLCT state of RuII(bpy)3 and RuII(bpy)2-E-Ph-E-Ipa also show the importance of including surroundings in the model for complexes with unsaturated substituents. In contrast to the parent RuII(bpy)3 complex which has a net spin of ca. one at the Ru centre in both gas phase and when surroundings are included, it is necessary to include surroundings to obtain a state of MLCT character for RuII(bpy)2bpy-E-Ph-E-Ipa. By evaluating the spin density of the complex optimized with explicit counter ions using a single point PCM acetonitrile calculation, the net spin at Ru is raised to 0.9 from as low as 0.1 in gas phase without counter ions. Similarly, the description of the formally oxidized Ru(III) dyes containing unsaturated rods requires inclusion of chemical environment to give a correct model. For instance, the calculated spin density at the Ru core goes from 0.05 to 0.96 for RuIII(bpy)2-E-Ph-E-Ipa in gas phase and in acetonitrile with two PF6 counter ions, respectively, while the corresponding values for RuIII(bpy)3 are 0.96 in both models. Hence, we don’t have a Ru(III) core in the bare gas phase model of the E-Ph-E-Ipa containing complex. Experimentally, the oxidation potentials of RuII(bpy)3 and RuII(bpy)2-E-Ph-E-Ipa are highly similar.71 The calculated oxidation energy, i.e. E[Ru(III)]-E[Ru(II)] of the two dyes obtained when including surroundings are highly similar (within ±0.08 eV), while the gas phase results differ with 2 eV. Hence, the calculations on RuII(bpy)3 and RuII(bpy)2-E-Ph-E-Ipa suggest that the calculated electronic properties are sensitive to the surroundings for dyes carrying unsaturated substituents, while calculations on “pure” Ru polypyridyl complexes do not necessarily require the inclusion of chemical environment.
3.3.2 Ru\textsuperscript{II}(tpy)\textsubscript{2} functionalized with phenylene spacer and carboxylic or phosphonic acid anchor (IV)

The dyes most commonly used in photoelectrochemical applications are anchored to the metal oxide via carboxylic acid or phosphonic acid groups that bind to the surface.\textsuperscript{72} Carboxylic acid anchor groups are known to give good electronic coupling over the dye-substrate interface,\textsuperscript{6} while phosphonic acid binds more strongly to the surface.\textsuperscript{73,74} In order to investigate the effect of connecting anchor and spacer groups to the Ru\textsuperscript{II}(tpy)\textsubscript{2} chromophore in terms of structural, electronic and spectral properties, DFT and TD-DFT calculations with and without PF\textsubscript{6}\textsuperscript{–} ions in the model were performed. Ru\textsuperscript{II}(tpy)\textsubscript{2} was functionalized with the anchor group directly attached at the 4’-position of the central pyridyl of one of the tpy ligands (Ru\textsuperscript{II}(tpy)\textsubscript{2}-COOH and Ru\textsuperscript{II}(tpy)\textsubscript{2}-PO\textsubscript{3}H\textsubscript{2}) or with a rigid phenylene spacer inserted in between the chromophore and the anchor group (Ru\textsuperscript{II}(tpy)\textsubscript{2}-Ph-COOH and Ru\textsuperscript{II}(tpy)\textsubscript{2}-Ph-PO\textsubscript{3}H\textsubscript{2}). Effects of surroundings were included in the calculations as two explicit PF\textsubscript{6}\textsuperscript{–} ions, and the ion-induced effects on geometry and electronic structure were examined. In the fully optimized B3LYP/LANL2DZ structures, the shortest Ru-P distance is 5.7 Å, that can be compared to the 6.1-6.6 Å in the [Ru\textsuperscript{II}(tpy)\textsubscript{2}]PF\textsubscript{6}\textsuperscript{–}\textsubscript{2} crystal structure,\textsuperscript{75} which was used for guidance when constructing the starting structures. The two PF\textsubscript{6}\textsuperscript{–} ions were placed so that interaction between the two ions, as well as with the surface of TiO\textsubscript{2} used in later applications, was prevented. In the resulting systems most of the positive charge is localized at the ruthenium core, while the negative charge is spread over the counter ions. The combined systems form a vectorial structure with linear axis through N-Ru-N-(Ph-)C/P, with the anchor groups oriented such that the oxygen double bond is in plane with the connecting conjugated moiety (tpy or Ph) and the phenylene spacer is twisted ca. 30° out of the tpy plane. Overall, the geometrical changes in the parent Ru\textsuperscript{II}(tpy)\textsubscript{2} when connecting the individually optimized parts (chromophore, spacer, anchor, counter ions) are small. The ions slightly distort the perfectly planar tpy planes found in bare Ru\textsuperscript{II}(tpy)\textsubscript{2}, and they change the bonds in the tpy framework with maximum 0.01 Å. In addition, the Ru-N distances generally become 0.01 Å shorter when including ions in the model. Also the connection of chromophore, spacer, and anchor result in bond distance changes of maximum 0.01 Å compared with bare Ru\textsuperscript{II}(tpy)\textsubscript{2}. Therefore, in terms of geometrical structure, the system can almost be viewed as separate building blocks that only change their relative orientation upon connection. These findings are later utilized when creating models of dye-sensitized systems.

The electronic structure and electronic excitations were calculated with B3LYP/VD(T)Z (the basis set is described in Chapter 2). In the electronic structure of unsubstituted Ru\textsuperscript{II}(tpy)\textsubscript{2}, which has many similarities to that of Ru\textsuperscript{II}(bpy)\textsubscript{3}, the three HOMOs are of Ru 4d-orbital character and the main
character of the LUMOs is ligand pyridyl-π*. The PF$_6^-$ ions disrupt the symmetry of the system such that there is an energetic separation of previously degenerate MOs. Moreover, the PF$_6^-$ ions induce an energy shift of all MOs to higher energies, which is similar to the effect of including PCM solvent. For instance, the HOMO for Ru$^{II}$(tpy)$_2$ is shifted from −11.2 eV to −6.4 eV by including counter ions with VD(T)Z, and to −6.2 eV in acetonitrile solvent calculated as a standard PCM single point calculation with VD(T)Z. This energy level shift will be important for the modeling of dye-sensitized systems. Moreover, the HOMO-LUMO gap is slightly decreased (0.2-0.4 eV) for the systems by inclusion of counter ions.

![Figure 10. The B3LYP/VD(T)Z HOMO and LUMO of Ru$^{II}$(tpy)$_2$-Ph-COOH calculated with and without two explicit PF$_6^-$ ions.](image)

The HOMO-LUMO gap is also decreased 0.01-0.04 eV by functionalization with anchor and spacer groups due to mixing of anchor and spacer MOs with chromophore MOs in the HOMO-LUMO region in the combined system. The character of the HOMO and LUMO of Ru$^{II}$(tpy)$_2$-Ph-COOH and Ru$^{II}$(tpy)$_2$-Ph-PO$_3$H$_2$ is found to be strongly affected by the inclusion or exclusion of counter ions in the calculation, similarly to the discussion in Section 3.3.1 of the MOs for Ru$^{II}$(bpy)$_3$E-Ph-E-Ipa. In the electronic structures with ions, the three top HOMOs of 4d-orbital type are largely unaffected by substitution at the 4’-position, both by anchor and spacer groups, which is shown for the HOMO of Ru$^{II}$(tpy)$_2$-Ph-COOH in Figure 10 (left). In the LUMO, anchor and spacer fragment MOs mix with the MO levels of the parent Ru$^{II}$(tpy)$_2$ complex, such that there is a delocalization of the tpy-π* onto the phenylene spacer and in Ru$^{II}$(tpy)$_2$-Ph-COOH also down to the carboxyl anchor (Figure 10, left). However, without counter ions, the orbitals of the phenylene unit mix into the HOMO, which contains a mixture of chromophore, spacer and anchor contributions. The LUMO has instead only tpy-π* character on the unsubstituted tpy ligand (Figure 10, right). These two different HOMO and LUMO distributions will result in very different predictions for the direction of HOMO→LUMO excitation.
The simulated absorption spectra in the 400-650 nm region for Ru\textsuperscript{II}(tpy)\textsubscript{2}-Ph-COOH and Ru\textsuperscript{II}(tpy)\textsubscript{2}-Ph-PO\textsubscript{3}H\textsubscript{2} show that with counter ions all excitations result in metal-to-ligand or metal-to-ligand-spacer-anchor excitations, and without counter ions the lowest energy excitation is dominated by metal-spacer-anchor-to-ligand transitions, thus indicating excitations in opposite directions. Hence by including or excluding surroundings in the calculation different interpretations of the photoexcitation process is obtained. In a dye-sensitized metal oxide system, an excitation away from the surface which is indicated by the results without ions is clearly unwanted in terms of photoinduced electron injection. Conversely, the calculations with counter ions indicate that anchor and spacer can mediate the electron transfer from chromophore to the surface by the delocalization of tpy ligand, spacer and anchor π*-orbital character in the LUMO.

The inclusion of explicit counter ions in the calculations shifts all the key spectral features in the 400-650 nm region of all the substituted complexes towards longer wavelengths. For the functionalized chromophores, the overall spectral features are preserved compared with the spectrum of the parent chromophore but generally the features are shifted towards longer wavelengths and the relative intensity of excitations are changed. However, due to the high degree of similarity between the calculated spectra the results indicate that an experimental spectral distinction between the complexes would be difficult.

The inclusion of explicit counter ions can be used as an alternative to using PCM solvent models to stabilize the positive charge, which is important when studying Ru(II) polypyridyl systems with unsaturated substituents. The results on OPE functionalized Ru\textsuperscript{II}(bpy)\textsubscript{3} indicate that the best approach is to include explicit counter ions and a continuum solvent model. For calculations on very large systems (see Chapter 5 and Paper IV) however, the use of only counter ions has technical advantages because it has proven difficult to run very large PCM calculations. The effect of using explicit ions appears to be primarily electronic and not geometrical.

3.4 Performance of the computational methods (I-IV)

When comparing the B3LYP/LANL2DZ optimized structures of the investigated Ru(II) polypyridyl complexes with X-ray crystal structure data, the Ru-N bond lengths are consistently overestimated with 0.01-0.08 Å.\textsuperscript{66,75,77-82} However, although the Ru-N distances are too long, the conformations that are predicted as the most stable are highly similar to the corresponding crystal structures (with one exception). The Ru-N distances are predicted to be longer for py ligands than for bpy and shortest for tpy; Ru-N(py) (2.10-2.14 Å) > Ru-N(bpy) (2.08-2.13 Å) > Ru-N(tpy) (2.01-2.11 Å) in agreement with the crystal structure data.\textsuperscript{66,77-82} Furthermore, basis set tests for geometry
optimization of Ru\textsuperscript{II}(tpy)\textsubscript{2} performed using B3LYP and the LANL2DZ or SDD effective core potentials and associated basis set on Ru, and SDD, D95V, 3-21G\textsuperscript{*} or 6-31+G(d,p) on the remaining atoms, showed that all basis sets slightly overestimate the Ru-N distances compared to available crystal structures,\textsuperscript{75,81,82} but that the calculated N-Ru-N angles are in all cases highly similar to the crystal structure data.

The TD-B3LYP/LANL2DZ simulations of absorption spectra predict that d→π*(bpy/tpy) MLCT excitations are found at wavelengths between 400 and 600 nm, while d→π*(py/bpy/tpy) MLCT transitions mixed with d→d components are found at 300-400 nm and LC π→π* transitions are found at wavelengths below 300 nm. The overall agreement between experimental spectra in acetonitrile and calculated gas phase spectra is good for unsubstituted Ru(II) polypyridyl complexes, but some discrepancies are seen in the 400-600 nm region. For the majority of the complexes, the MLCT absorption maximum is reproduced to within 20 nm (energetically overestimated). However, for Ru\textsuperscript{II}(tpy)\textsubscript{2} and Ru\textsuperscript{II}(bmp)\textsubscript{2} the predicted absorption maximum is ca. 50 and 30 nm lower than the experimentally determined values in acetonitrile solvent. Both simulated spectra contain a low intensity transition and a zero intensity transition closer to the experimental maximum that could possibly be accessible by removal of symmetry by surroundings and/or thermal effects. Indeed, calculations for Ru\textsuperscript{II}(tpy)\textsubscript{2} including explicit counter ions improve the agreement with experimental results, but inclusion of solvent using the PCM model does not change the results. Generally, gas phase and PCM data are highly similar for the pure complexes.

Basis set test of the shapes and features of the absorption spectra of Ru\textsuperscript{II}(tpy)\textsubscript{2} using LANL2DZ, VD(T)Z, and 6-31+G(d,p) with LANL2DZ on Ru in all three cases, showed that the spectra are highly similar. The excitations are slightly shifted (6-12 nm) to shorter wavelengths when using VD(T)Z compared to LANL2DZ, and the VD(T)Z ECP/basis set with ECPs on all non-hydrogens performed highly similar (±3 nm) to the large all-electron basis set 6-31+G(d,p) which includes both diffuse and polarization functions. In Paper III the effects of ECP/basis set combination and XC functional on the absorption threshold are investigated for Ru\textsuperscript{II}(bpy)\textsubscript{3}-E-Ph-E-Ipa using the PCM model for acetonitrile. With B3LYP and LANL2DZ, CEP-31 and -121 as well as SDD, the lowest energy excitation varies from 537 to 554 nm (gas phase 783-816 nm). Using LANL2DZ, the B3LYP and PBE1PBE hybrid functionals give similar results (530 and 500 nm) and the pure GGA functionals HCTH and BLYP (740 and 720 nm) give similar results. This difference can be explained by the fact that pure GGA functionals generally predicts smaller HOMO-LUMO gaps than hybrid functionals.\textsuperscript{83,84} It appears that it is important to include counter ions in the model or to account for bulk solvent effects using the PCM solvent model in particular when investigating functionalized dyes, whereas the results are less dependent on the specific hybrid functional and ECP/basis set combination used.
4 Titanium dioxide nanoparticles

4.1 Nanocrystalline titanium dioxide

Titanium dioxide (TiO₂) is one of the most studied metal oxides due to its many technological applications. This semiconductor material is used e.g. in heterogeneous catalysis, as a photocatalyst, in solar cells, as gas sensors, as white pigment, and as biomaterials. Besides its photocatalytic abilities, the main advantages of TiO₂ are that it is stable in different chemical environments, non-toxic and inexpensive. TiO₂ is a material with several crystal forms of which two, rutile and anatase, have been extensively studied. The rutile crystal structure is usually considered the thermodynamically most stable form of TiO₂, and anatase the more probable phase in particles of size below 10-13 nm. In dye-sensitized solar cells porous nanocrystalline TiO₂ films are used, which consist of an interconnected network of nanosized TiO₂ particles. The porous films exhibit increased reactivity as well as special optical and electronic properties which are coupled to the small size and large surface-area-to-bulk ratio. TiO₂ is a wide band gap material, with a band gap of 3.0-3.2 eV, which means that it only absorbs UV light.

In terms of theoretical calculations, TiO₂ is one of the most extensively studied transition metal oxides, and both bulk, surface and molecular properties of TiO₂ have been explored in the literature. The size and complexity of nanocrystalline TiO₂ impose significant computational challenges for quantum chemical modeling of TiO₂ nanoparticles, in both the choice of methods and chemical models. The computational cost grows quickly with increasing model size, since every TiO₂ unit adds 38 electrons to the system. Therefore, the majority of studies concern either calculations on small cluster models (bare or with saturation and/or charge embedding) or calculations with periodic boundary conditions. Periodic calculations have an intrinsic advantage in automatically providing continuous electronic structure bands and a stabilization of the surface structure by the repetition of the unit cell in two dimensions. However, for modeling of sensitization of nanoparticles with large dye molecules, periodic calculations can be computationally very expensive since the model then requires very large unit cells to avoid undesirable dye-dye interaction across the periodic cell boundaries. With the clus-
ter approach, the accommodation of large dyes is relatively unproblematic. However, the use of small cluster models in surface studies is often associated with termination problems requiring saturation of dangling bonds or the use of point charge embedding to stabilize the model and impose some boundary conditions. With large, bare cluster models it would be possible to directly capture various types of surface motifs and other properties typical of a nanoparticle. Very large models, from a computational perspective, are necessary in order to capture the electronic effects, which means going from finite MO levels to continuous bands. Several papers in the literature deal with small TiO$_2$ clusters calculated with quantum chemical methods, while the studies on medium and large clusters are few due to the computational cost.

### 4.2 Anatase cluster models

Quantum chemical modeling of TiO$_2$ nanoparticles using large cluster models have, besides an early semi-empirical study on hydrated TiO$_2$ clusters started to appear in recent years using Hartree-Fock and DFT methods. In the approach used in this thesis, nanocrystalline TiO$_2$ is modeled by large, bare anatase cluster models fully optimized with DFT methods starting from the anatase crystal structure. The anatase cluster models are constructed by cutting the cluster models from a large cluster obtained by expansion of the anatase crystal structure unit cell (12 atoms in all three dimensions). Ti and O atoms are removed such that the resulting cluster is stoichiometric, charge neutral, and with as high coordination of every Ti and O atom as possible. The majority of nanosized models studied here have a large anatase (101) surface section, which is the most stable surface of anatase. The cluster models are fully optimized as a bare cluster without any saturation of dangling bonds or charge embedding applied. The large models require efficient computational methods, and PW/VSZ, the PW86PW91 functional in combination with a minimal STO basis set with large frozen core, or B3LYP/VDZ, the B3LYP hybrid functional in combination with a double-zeta basis set with large ECP, are used for geometry optimization.

### 4.3 Calculated structural and electronic properties (V)

The properties of six anatase nanoparticle models based on this approach containing 16, 28, 38, 46, 60, and 68 TiO$_2$ units have been studied. In the anatase bulk structure every Ti atom is coordinated by six O atoms, and every O atom by three Ti atoms. In the unrelaxed nanoparticle models, a large fraction of the atoms are under-coordinated atoms, e.g. in (TiO$_2$)$_{16}$ 88% are under-coordinated and in (TiO$_2$)$_{60}$ the number is 53%. The large number
of under-coordinated atoms results in a lack of structural stabilization and a high degree of dangling bonds, which in turn result in substantial relaxation upon geometry optimization. The anatase crystal form is largely maintained intact in the relaxed cluster models obtained with both methods. However, the two methods used for geometry optimization results in two slightly different structure types. In the PW/VSZ structures, the coordination is totally maintained. However, the B3LYP/VDZ method produces geometries with a high degree of surface reorganization and with lower total coordination than the crystal connectivity. Optimization leads to increase of the number of under-coordinated atoms, and formation of Ti=O surface species. The Ti=O surface species are not seen in the PW/VSZ structures. The average Ti-O bond lengths of the nanosized clusters decrease from 1.95 Å in the unrelaxed bulk structure to 1.91 Å and 1.89 Å with the B3LYP/VDZ and PW/VSZ methods, respectively. In the crystal bulk structure there are two different bond lengths, which relaxes to Ti-O bond lengths spread over the range 1.5-2.3 Å in the B3LYP/VDZ optimized structures and 1.7-2.1 Å in the PW/VSZ structures.

In addition to the nanoparticle set of models, a set of smaller cluster models were constructed, with anatase structure motif when possible, to be able to study how electronic properties evolve with cluster size. The stabilization energy of this set (n=1-68) of models, calculated with B3LYP/VDZ as the total energy per TiO₂ unit relative to the energy of the free TiO₂ molecule, is highly similar for the B3LYP/VDZ and PW/VSZ structures of a given size.

Electronic structure calculations performed on a small test system, comprising three (TiO₂)₅ geometries, using several different basis sets and functionals showed the commonly accepted knowledge concerning the prediction of HOMO-LUMO gaps, that Hartree-Fock produce large gaps (12.9 eV), pure DFT functionals small gaps (2.7 eV) and hybrid DFT functionals intermediate gaps (4.8 eV), with calculated HOMO-LUMO gaps of a selected (TiO₂)₅ geometry given in parenthesis. Moreover, it has been shown that B3LYP predict metal oxide band gaps in good agreement with experimental values. Therefore, the electronic structures of the nanocrystals were calculated with B3LYP and the VDZ and VD(T)Z basis sets which are affordable even for the largest nanocrystals.

Although the nanoparticle models are finite clusters and not a bulk crystal, i.e. the electronic structure consists of finite MO levels and not continuous bands, we often use the language used for solids. The effective density of states (DOS), constructed from the discrete MO levels, shows a broad filled valence band and a broad empty conduction band that are separated by a defect-free band gap. The top of the valence band essentially has oxygen 2p orbital character, whereas the conduction band is mainly of titanium 3d orbital character. The Ti=O defect sites present in the B3LYP/VDZ structures do not introduce any states in the band gap region. Instead, the HOMO-LUMO gap is larger, generally 0.4 eV or more for the B3LYP/VDZ struc-
tures, than for the less reorganized PW/VSZ structures. Hence, the calculations show that the HOMO-LUMO gap is changed with different connectivity of the atoms. Moreover, the size of the band gap varies with cluster size, with a general slow decrease in band gap as the size of the nanosized systems increase (spherically) towards quasi-bulk-like electronic properties. The width of HOMO-LUMO gap and the lowest energy excitation (TD gap) are highly similar for the VDZ and VD(T)Z basis sets. However, the positions of the HOMO and LUMO levels appear to be sensitive to basis set choice. The position of the HOMO and LUMO levels (or valence and conduction band edges) is higher for the VDZ basis set than for the VD(T)Z basis set.

4.4 Performance of the computational methods (V)

The basis set and functional tests performed on the small (TiO$_2$)$_5$ test system comprising three different isomers, revealed that the structure with the most Ti=O bonds was the most stable with the majority of methods tested. The PW/VSZ method favors cluster geometries with many Ti-O single bonds. However, for this minimal basis the calculated Ti-O bond lengths are not basis set converged when compared to the larger double-zeta (DZ) and triple-zeta plus polarization (TZP) basis sets which produce substantially shorter bond lengths. A similar effect is seen for the LANL2MB basis set, which also is a minimal basis, in combination with B3LYP. In terms of average and single Ti-O bond lengths, the B3LYP method performs highly similar with the VDZ basis set as with the tested all-electron 6-31G and 6-311G basis sets. However, B3LYP/VDZ appears to predict shorter Ti=O bonds than the all-electron basis sets.

The calculated nanocrystal structural data can also be validated by comparison with experimental or high level calculated Ti-O bond lengths for a single TiO$_2$ gas phase molecule and for anatase bulk data. For a single TiO$_2$ gas phase molecule, the B3LYP/VDZ geometry slightly underestimates the Ti-O distance, calculated to be 1.603 Å compared to the experimental 1.62±0.08 Å$^{95}$ and B3LYP/6-31G(d,p) calculated to be 1.630 Å, while PW/VSZ overestimates the bond length (1.67 Å). For anatase bulk, the two Ti-O bond lengths are slightly overestimated by periodic B3LYP/VDZ calculations, 1.958 and 1.983 Å$^{73}$ compared to the crystal structure values 1.934 and 1.979 Å$^{92}$ or 1.937 and 1.965 Å$^{95}$. These calculated B3LYP/VDZ bulk bond lengths compare equally well to experimental values as those calculated with B3LYP and the larger modified 6-31G basis set by Beltran et al. (1.951 and 1.997 Å).$^{97}$ A similar comparison for the PW/VSZ method is not possible, since no periodic calculations using the PW/VSZ method on the anatase bulk are available.
The B3LYP/VDZ electronic bulk band gap is 3.4 eV obtained by periodic calculations\textsuperscript{73} which is a slight overestimation of the experimental band gap of 3.2 eV\textsuperscript{96} for anatase bulk. Moreover, the experimental band gap of 2.4 nm TiO\textsubscript{2} nanoparticles has been reported to be 0.2 eV larger than the bulk band gap.\textsuperscript{59} When comparing the B3LYP/VDZ HOMO-LUMO gaps for the three largest nanocrystals, which are 3.7-4.1 eV for the PW/VSZ structures and 4.6-4.9 eV for the B3LYP/VDZ structures, with a band gap of ca. 3.6 eV which could be expected for a 2.4 nm nanoparticle within the given method, it appears that the HOMO-LUMO gaps of both the PW/VSZ and B3LYP/VDZ structures are somewhat overestimated. The calculated optical band gaps, on the other hand, are 3.3-3.6 eV for the PW/VSZ structures.

Although the calculated electronic and optical gaps are relatively insensitive to basis set choice, the positions of the valence and conduction band edges, \textit{i.e.} the HOMO and LUMO levels, are more basis set sensitive. According to the (TiO\textsubscript{2})\textsubscript{5} test set, the HOMO-LUMO gaps calculated with the efficient VDZ and VD(T)Z basis sets are highly similar to those of the all-electron 6-311+(2df,p) basis sets. However, the position of the HOMO and LUMO levels using the VD(T)Z basis set are closer to the 6-311+(2df,p) levels than the positions obtained with VDZ, and therefore VD(T)Z appears to be better at describing the electronic structure of the TiO\textsubscript{2} nanoparticle systems.

4.5 The (TiO\textsubscript{2})\textsubscript{n}, n=38, 46 and 60 chemical models (IV-VII)

Three of the nanoparticle models, which are shown in Figure 11, are used for dye-sensitization in Papers IV-VII. These three models exhibit slightly different structural and electronic features. Both the (TiO\textsubscript{2})\textsubscript{46} and (TiO\textsubscript{2})\textsubscript{38} models that are used in Papers IV-V and VII, respectively, were obtained by geometry optimization with the B3LYP/VDZ method, while the (TiO\textsubscript{2})\textsubscript{60} model used in Paper VI was obtained with PW/VSZ.

The (TiO\textsubscript{2})\textsubscript{38} model has a relatively large anatase (101) surface section, and the typical anatase structural patterns, and the saw-tooth shape of the anatase (101) surface can be seen after optimization. In the (TiO\textsubscript{2})\textsubscript{38} starting structure already 67% of the atoms are under-coordinated and after optimization with B3LYP/VDZ this fraction has increased to 78%. The maximum atom distance is 16.9 Å although the model only contains 38 TiO\textsubscript{2} units, but it has a thin slab thickness. Therefore, the model only has six six-fold coordinated Ti atoms in the starting structure and only two remains after relaxation.

The (TiO\textsubscript{2})\textsubscript{46} model has a smaller (101) surface section compared to (TiO\textsubscript{2})\textsubscript{38}, however, the slab thickness is doubled, which makes this model
rather spherical. In the (TiO\(_2\))\(_{46}\) starting structure 59% of the atoms are under-coordinated which is increased to 73% by optimization with B3LYP/VDZ, which also reduces the six-fold coordinated Ti atoms from twelve to six. After optimization it still has a bulk-like core, with six six-fold coordinated titanium atoms and a number of three-fold coordinated oxygens. Due to the spherical shape, the maximum atom distance in the (TiO\(_2\))\(_{46}\) model is of the same size as that of the (TiO\(_2\))\(_{38}\) model although 24 atoms have been added.

![Figure 11. The optimized structure of the (TiO\(_2\))\(_{38}\), (TiO\(_2\))\(_{46}\), and (TiO\(_2\))\(_{60}\) models viewed from two angles. The number of layers building up the slab thickness of the models is highlighted by dashed lines.](image)

The (TiO\(_2\))\(_{60}\) model has a small anatase (101) surface section, and has been extended even one more layer compared to the (TiO\(_2\))\(_{46}\) model. As the (TiO\(_2\))\(_{38}\) model was constructed to have as large (101) surface area as possible, the (TiO\(_2\))\(_{60}\) model was constructed to be as deep as possible. The maximum atom distance is 18.8 Å in this model. Since this model was optimized using PW/VSZ it is not highly reorganized, and the crystal bulk connectivity and the high number of six-fold coordinated Ti atoms (22) are preserved after optimization.

The spacing between the MO levels in the lower unoccupied region, which indicates the transition from cluster to crystal is on average 23, 20, and 30 meV for the (TiO\(_2\))\(_{38}\), (TiO\(_2\))\(_{46}\), and (TiO\(_2\))\(_{60}\) models, respectively, at the B3LYP/VD(T)Z level including the lowest 30 unoccupied MO levels in the analysis. A small enough level splitting is important for the analysis of the electronic coupling between dye and TiO\(_2\) in the following chapter.
5 Dye-sensitized TiO₂ nanoparticles

Photoinduced charge separation in dye-sensitized nanostructured TiO₂ occurs via surface electron transfer across the dye-TiO₂ interface. Following initial excitation of the dye by illumination with visible light, the photoexcited electron is injected from the dye into the conduction band of TiO₂. For efficient charge separation, favorable geometrical and electronic coupling between the dye and TiO₂ is required. In the two previous chapters several aspects of the individual parts of dye-sensitized systems have been investigated and the quantum chemical modeling of the parts has been described. In this chapter, the dye and the TiO₂ nanoparticle are combined, and the focus of the discussion is on the geometrical and electronic coupling between the parts in the combined system. In addition, aspects of the modeling of the large systems, which involves three slightly different approaches to obtain the geometry of the dye-TiO₂ systems, are discussed. The interfacial electronic coupling is estimated from the calculated electronic structure of the combined system using a simple MO mixing model. Estimates of electron injection times are obtained from the calculated electronic couplings.

5.1 Adsorption of carboxylic and phosphonic acid (V)

Important to the function of a dye-sensitized devise is a strong and stable binding of the dye to the surface via anchor groups. Two of the most commonly used anchor groups for attachment of ruthenium dyes on the TiO₂ surface are carboxylic and phosphonic acid anchor groups. The binding of the acids can occur through a variety of binding modes. What binding modes that are possible and what mode that will be the most common depends on the structure of the anchor group, the surface geometry and the surrounding environment (e.g. solvent and pH). The binding to TiO₂ can occur either through mono-, bi-, and in the case of –PO₃H₂ also tri-dentate binding, which is determined by how many oxygen atoms the adsorbate use to bind to surface Ti atoms. Some examples of binding modes are shown in Figure 12. The two examples of bidentate modes are both dissociative adsorption of the acid, i.e. bonds in the acid have been broken upon adsorption. In the two examples of monodentate binding modes, the acids are non-dissociatively adsorbed, and the hydroxyl groups have formed hydrogen bonds to surface oxygen atoms.
Both experimental and periodic computational results show that phosphonic acid binds stronger to the surface than carboxylic acid.\textsuperscript{73,74,101} According to computational studies of the adsorption of the two acids on a clean anatase (101) surface in gas phase using a periodic slab model, monodentate binding modes are energetically favored over bidentate binding.\textsuperscript{73,100} In order to investigate the effects of using nanoparticle cluster models on anchor group binding, the monodentate binding modes of HCOOH and HPO\textsubscript{3}H\textsubscript{2} found to be favored in the periodic study were transferred to the (TiO\textsubscript{2})\textsubscript{46} model which has a anatase (101) surface section large enough to accommodate the phosphonic acid binding footprint. The entire systems were fully optimized with B3LYP/VDZ. Adsorption on the nanoparticle does not only result in changes of the local structure around the adsorption site of the TiO\textsubscript{2} model, but also in a slight reorganization that progresses through the Ti-O framework all the way to the opposite side of the cluster. Compared to the periodic results, there is a larger bond rearrangement for HCOOH, especially involving the hydroxyl group and the hydrogen bond to the surface. Although the internal anchor bonds are highly similar to the periodic results in the case of HPO\textsubscript{3}H\textsubscript{2} adsorption, the anchor-TiO\textsubscript{2} bonds are generally shorter for both HCOOH and HPO\textsubscript{3}H\textsubscript{2} indicating a stronger bonding in the cluster model.

The calculated absorption energies are 82 and 42 kcal/mol for phosphonic acid and carboxylic acid, respectively, for the nanoparticle. The corresponding periodic values are 49 and 29 kcal/mol. The differences in the adsorption strength also indicate a larger reactivity of the cluster surface compared to the periodic surface. In the electronic structure, the anchor group MO levels are well merged into the TiO\textsubscript{2} valence and conduction bands. Adsorption of the anchor groups does not introduce any levels in the band gap or shift or change the size of the band gap compared to the bare TiO\textsubscript{2} cluster.

5.2 Calculation of interfacial electronic coupling strengths

Ultrafast electron transfer across the dye-TiO\textsubscript{2} interface can occur when the coupling between the excited state of the dye (dye\textsuperscript{*}) and the conduction band of TiO\textsubscript{2} is strong. Assuming that the primary photoexcitation process
involves excitation from the HOMO to the LUMO of the dye, the electronic coupling between dye* and TiO₂ conduction band is approximated by the degree of orbital mixing of the dye LUMO and the unoccupied TiO₂ levels. This approach is adopted from the Newns-Anderson model for adsorbates on surfaces. The electronic coupling is estimated by how much the LUMO of the dye changes in terms of energetic shift ($\Delta E$) and broadening ($\hbar \Gamma$) when interacting with TiO₂. This model is shown schematically in Figure 13. For a strong electronic coupling, dye LUMO orbital contributions can be found mixed with TiO₂ orbital contribution in many MO levels of the combined dye-TiO₂ system. A weak coupling corresponds to a few, energetically closely spaced MO levels with a high concentration of orbital contribution on the dye. All data required to quantify the shift and broadening is extracted from electronic structure calculations of the isolated dye and the combined dye-TiO₂ system.

Figure 13. Schematic illustration of the Newns-Anderson type model of electronic coupling of a photoexcited dye and the TiO₂ conduction band. The electronic coupling is described in terms of an energetic shift, $\Delta E$, and a broadening, $\hbar \Gamma$, of the dye* electronic levels.

In the electronic structure of the dye-sensitized system, the adsorbate portion, $p_i$, of every MO, $i$, with orbital energy, $\xi_i$, is extracted from the $n$ basis set expansion coefficients, $c_{ij}^\alpha$, centered on adsorbate atoms ($A$):

$$p_i = \frac{\sum_{j} (c_{ij}^\alpha)^2}{\sum_{j} (c_{ij}^\alpha)^2}.$$  \hspace{1cm} (19)

The MOs that contain adsorbate portions equivalent to that of the free adsorbate LUMO, the LUMO(ads) levels, are identified and collected such that $\Sigma p_i \approx 1$. The center of the LUMO(ads) distribution, $E_{LUMO(ads)}$, is then obtained by a weighted average,
and the adsorption induced energy shift by

$$\Delta E = E_{\text{LUMO}}(\text{ads}) - E_{\text{LUMO}}(\text{free ads}),$$

where the value of $E_{\text{LUMO}}(\text{free ads})$ is obtained from a separate electronic structure calculation of the free adsorbate. The width of the broadening, $h\Gamma$, is taken as the mean deviation of the LUMO(ads) levels,

$$h\Gamma = \sum_i p_i |E_i - E_{\text{LUMO}}(\text{ads})|$$

From the calculated electronic coupling strength the electron injection time between dye and TiO$_2$ can be estimated through $\tau(\text{fs}) = 658/h\Gamma$ (meV).

5.3 Perylene dyes on TiO$_2$ (VI)

The organic chromophore perylene, Pe, (see Figure 14) is a suitable system for both experimental and theoretical investigations of heterogeneous electron transfer to TiO$_2$. The dye absorbs light in the visible region, the singlet ground state falls into the band gap of TiO$_2$, and there is little spectral overlap of the dye states involved in the photoexcitation and the subsequent electron transfer reaction (Pe, Pe$^*$ and Pe$^-$). Moreover, the excited state of the dye is sufficiently high above the TiO$_2$ conduction band edge to be in the so-called wide-band limit, where the electron transfer rate is controlled by the electronic coupling strength.$^{103–105}$ The perylene chromophore was used to test the applicability of the calculation of electronic coupling strength from the electronic structure and the ability to predict heterogeneous electron injection times.

Three substituted perylene dyes were adsorbed onto TiO$_2$, by a carboxylic acid anchor group directly attached to the perylene molecule (Pe–COOH), via a saturated ethylene spacer (Pe–CH$_2$–CH$_2$–COOH), or via an unsaturated ethenylene spacer (Pe–CH=CH–COOH). A schematic illustration of the steps used to construct the dye-sensitized systems is shown in Figure 14, and is outlined as follows: (I) The isolated perylene dyes were optimized and the electronic structure and the lowest singlet excitations were calculated using B3LYP/6-31G(d,p). (II) The TiO$_2$ nanoparticle model, (TiO$_2$)$_{60}$, was optimized separately using PW/VSZ. (III) A surface section containing five Ti atoms was cut out of the anatase (101) surface of the (TiO$_2$)$_{60}$ model and the dangling bonds were saturated with hydrogen and hydroxyl saturators, resulting in a (TiO$_2$)$_5$(H$_2$O)$_5$ cluster. The dyes were adsorbed onto the small cluster by attachment of the carboxylic acid in a bridging bidentate adsorption mode, and the resulting complex was optimized with PW/VSZ with the
saturators and the atoms to which they are attached kept fixed, relaxing the dye and the local TiO$_2$ surface area in the vicinity of the anchor group attachment. (IV) The small cluster with the dye was re-introduced into the large cluster and the electronic structure of the dye-sensitized system was calculated with B3LYP/VD(T)Z.

Figure 14. The perylene molecule with the site of anchor and spacer attachment indicated by an X substituent and a schematic illustration of the geometry optimization scheme used in the modeling of the perylene-sensitized TiO$_2$ systems.

The perylene molecule has a conjugated planar structure, and the lowest singlet excitation is a HOMO→LUMO excitation. The calculated HOMO and LUMO shown in Figure 15 are of π orbital character, which is delocalized over the entire Pe framework. The distribution of orbital character in the HOMO is largely maintained when attaching anchor and spacer groups. However, in the LUMO of Pe–COOH and Pe–CH=CH–COOH, the orbital character is delocalized onto the anchor and spacer, an effect that is not seen for the saturated spacer in Pe–CH$_2$–CH$_2$–COOH. Moreover, a red-shift of the lowest singlet excitation is seen for Pe–COOH and Pe–CH=CH–COOH compared to the parent chromophore due to a stabilization of the LUMO, similar to what was seen for the attachment of conjugated anchor and spacer groups to Ru(II) polypyridyl dyes in Section 3.3.

In the calculated interfacial electronic structures of the Pe dye-sensitized TiO$_2$ systems, the dye HOMO is located in the middle of the TiO$_2$ band gap and the LUMO(ads) is distributed over a number of mixed MO levels about 0.5-2 eV above the TiO$_2$ conduction band edge. For Pe–COOH and Pe–CH=CH–COOH, the LUMO(ads) levels are located closer to the edge than for Pe–CH$_2$–CH$_2$–COOH. In Figure 15, a selected LUMO(ads) level is shown for each of the systems Pe–COOH–(TiO$_2$)$_{60}$ and Pe–CH=CH–COOH–(TiO$_2$)$_{60}$, which clearly shows the mixing of dye and TiO$_2$ orbital character, as well as the delocalization of the LUMO onto spacer and anchor.
Using the Newns-Anderson type approach to analyze the energetic broadening of the LUMO(ads) levels in the three systems, the calculated electronic coupling strengths are 139, 102 and 20 meV for Pe–COOH, Pe–CH=CH–COOH and Pe–CH₂–CH₂–COOH, respectively. Converting the calculated coupling strength to estimated surface electron transfer times results in 4.7 (Pe–COOH), 6.5 (Pe–CH=CH–COOH) and 33 (Pe–CH₂–CH₂–COOH) femtoseconds (fs). Hence, in all three cases, the electron injection times are calculated to be in the sub-100 fs regime. The calculated results can be compared to experimentally determined surface electron transfer times measured for directly comparable systems, i.e. perylene dyes adsorbed on nanostructured TiO₂ under ultra-high vacuum conditions, studied by pump-probe femtosecond transient absorption spectroscopy. These experiments measure electron injection times of 13 (Pe–COOH), 10 (Pe–CH=CH–COOH) and 57 fs (Pe–CH₂–CH₂–COOH). The calculated electron injection times are ca. a factor two too fast compared with experimental values. The calculations manage to capture the difference in electronic coupling strength due to the chemical nature of the spacer group. The –CH₂–CH₂– and –CH=CH– spacer groups separates the chromophore and surface with similar distance, but the surface electron transfer times differ by a factor of six. In the case of the unsaturated spacer group, the spacer moiety acts as a mediator for electron transfer between chromophore and TiO₂ by the LUMO delocalization which favors a strong electronic coupling. The saturated spacer group has a significantly weaker electronic coupling compared to the other two systems, due to the lack of delocalization of the LUMO(ads) levels.
The quality of the computational approach can further be assessed by comparing with experimentally determined level alignments of Pe dye levels and the TiO₂ conduction band. By a combination of ultraviolet photoelectron spectroscopy, X-ray photoelectron spectroscopy and linear absorption measurement, the energetics of the interface of DTB–Pe–COOH (where DTB indicates two tert-butyl substituents on Pe) adsorbed onto colloidal anatase films has been characterized. The ground state is estimated to lie 1.9 eV below the conduction band edge, and the excited donor state 0.8-0.9 eV above. The B3LYP/VD(T)Z//PW/VSZ calculated values for the adsorbate HOMO and LUMO(ads) in the Pe–COOH–(TiO₂)₉₀ system are −1.9 and +0.7 eV relative to the TiO₂ LUMO. Considering that the actual dye excited state is approximated by the LUMO, the agreement is almost too good.

5.4 Ru(tpy)₂ dyes on TiO₂ (IV)

By adsorption of Ru⁹⁺(tpy)₂ onto nanocrystalline TiO₂ via an anchor group attached to the 4'-position of the central pyridyl of one of the tpy ligands, control of the relative orientation of the chromophore and TiO₂ surface can be obtained which can be useful for various applications. For instance, by substitution of the hydrogen at the 4'-position of the other tpy ligand with an electron donor e.g. tyrosine or a carotenoid, linear donor-chromophore-acceptor complexes, which assures no interaction between donor and acceptor can be constructed. Although the excited state lifetime for Ru⁹⁺(tpy)₂ is generally much shorter than for instance the commonly used N3 dye, the excited Ru⁹⁺(tpy)₂ chromophore is known to efficiently inject electrons into TiO₂.

The effects of different anchor and spacer groups on the interfacial electronic structure between Ru⁹⁺(tpy)₂ dyes and the TiO₂ surface were investigated by DFT and TD-DFT calculations, in terms of analysis of the effective densities of states and calculation of the lowest electronic excitations. The Ru⁹⁺(tpy)₂ chromophore was anchored to the (TiO₂)₉₀ cluster model by carboxylic acid or phosphonic acid anchor groups directly attached to the 4'-tpy position or with a phenylene spacer group spatially separating the chromophore and the anchor group. Two explicit PF₆⁻ counter ions were included in the calculations of the combined systems to make the total system charge neutral in order to assure that the energy levels of the separate parts match each other when the systems are combined. Structural, electronic and spectral properties of the isolated dyes and their interaction with explicit PF₆⁻ counter ions have already been discussed in Section 3.3.2.

The scheme used to construct the geometries of the Ru⁹⁺(tpy)₂ sensitized systems is illustrated in Figure 16, and is essentially as follows: (I) The isolated dye molecules with two PF₆⁻ counter were fully optimized at the B3LYP/LANL2DZ level of theory. (II) The TiO₂ cluster model was opti
mized using B3LYP/VDZ. (III) The anchor groups were adsorbed onto the (TiO$_2$)$_{46}$ cluster model followed by a full optimization of the anchor-nanoparticle system using B3LYP/VDZ, as described in Section 5.1. (IV) The anchor-nanoparticle geometry (A) was then merged with the separately optimized dye-counter ion system (B) at the carboxylic carbon or phosphonic phosphorus atom. No further optimization was applied and the electronic structure and the lowest excitations were calculated with B3LYP/VD(T)Z.

![Figure 16. Schematic illustration of the scheme used to construct the Ru$^{II}$(tpy)$_2$-sensitized TiO$_2$.](image)

In a simple energetic level matching of the HOMO and LUMO of for example the separate Ru$^{II}$(tpy)$_2$–PO$_3$H$_2$ dye without counter ions (HOMO $-11.23$ eV and LUMO $-7.86$ eV) and (TiO$_2$)$_{46}$ cluster model (HOMO $-8.18$ eV and LUMO $-3.47$ eV), the dye LUMO is located just above the TiO$_2$ valence band. When adsorbing the doubly charged dyes on (TiO$_2$)$_{46}$ without counter ions, the dye levels are energetically maintained at the same energy as in the isolated dye case, however, all the TiO$_2$ levels are shifted ca. $-2$ eV. As a result of this displacement of the TiO$_2$ levels, the dye LUMO is brought closer to the unoccupied TiO$_2$ levels, but are still located in the band gap. Hence this molecular model does not provide an adequately correct picture to model injection from the dye LUMO into the TiO$_2$ conduction band. As mentioned in Section 3.3.2, when including explicit counter ions in the calculation of the isolated dye, the energetic position of the MO levels are raised. For the dye-sensitized systems when counter ions are included, the dye levels are energetically maintained, and the TiO$_2$ levels are qualitatively preserved in the positions for the bare cluster, and thus generate a more realistic description of the dye-sensitized system. Inclusion of explicit counter ions in the modeling shows that the description of the environment is important for dyes with net charge in order to obtain a realistic interfacial energy level alignment. This could possibly also be achieved by including the effects of surrounding in the form of PCM solvent, which also shifts the energetic position of the dye MOs and screens the negative charge as was previ-
ously mentioned in Section 3.3.1. However, such calculations proved technically challenging for these large systems.

In the Ru(II)(tpy)$_2$ sensitized (TiO$_2$)$_{46}$ systems, the three highest occupied dye MO levels, *i.e.* MOs of Ru 4d orbital character, are located in the central region of the TiO$_2$ band gap, and hence no mixing with the TiO$_2$ levels occur. The counter ions introduce occupied levels in the TiO$_2$ valence band and unoccupied levels well above the TiO$_2$ conduction band edge, and are thus unlikely to affect the photoexcitation and the electron injection processes. The LUMO for the dyes with phosphonic acid anchor, Ru(II)(tpy)$_2$–PO$_3$H$_2$ and Ru(II)(tpy)$_2$–Ph–PO$_3$H$_2$, mixes with the unoccupied TiO$_2$ levels, such that the resulting LUMO(ads) levels are located ca. 1 eV up in the TiO$_2$ conduction band. However, for the two dyes with carboxylic acid anchor, the energies of the LUMO from the isolated dye and the edge of the TiO$_2$ conduction band coincide, and therefore the lowest LUMO(ads) levels for Ru(II)(tpy)$_2$–COOH and Ru(II)(tpy)$_2$–Ph–COOH are located at the edge of the conduction band in a region with large TiO$_2$ level spacing. In this situation, the LUMO(ads) does not properly fulfill the criteria of being in the wide band limit, which probably makes the calculated interfacial electronic coupling more sensitive to the local geometry at the interface. In addition, activation via nuclear motion may play a more prominent role in limiting the surface electron transfer rate in these cases.$^{103,110}$

The calculated electronic coupling strengths for LUMO(ads) of the four systems show that the strength is significantly affected by both the choice of anchor group and the presence of spacer group. In agreement with previous experimental and computational findings, the carboxylic acid anchor facilitates a stronger electronic coupling to TiO$_2$ than the phosphonic acid.$^{73,74}$ According to the present calculations the phosphonic acid anchor group decreases the coupling by a factor of ca. 6 compared to the carboxylic acid, and insertion of a phenylene spacer decreases the coupling strength with a factor of ca. 3. The estimated electron injection times based on the electronic coupling of the dye LUMO are 10 (–COOH), 25 (–Ph–COOH), 62 (–PO$_3$H$_2$), 158 (–Ph–PO$_3$H$_2$) fs, and thus all in the sub-200 fs regime.

The calculated lowest excitation in the dye-sensitized systems are all of dye-HOMO→LUMO(ads) type. Interestingly, the third lowest excitations for the carboxylic acid containing dyes which have significant intensity, show that also excitations to the LUMO+1(ads) levels, *i.e.* levels that originate from LUMO+1 of the free dye, can be involved in the photoexcitation process. The calculated injection times for these levels are substantially longer than for LUMO(ads), 98 fs for Ru(II)(tpy)$_2$–COOH and >1 ps for Ru(II)(tpy)$_2$–Ph–COOH, due to a significantly weaker electronic coupling since there is no delocalization of the tpy–π* orbital onto the carboxyl anchor group.
5.5 The Ruthenium dye N3 on TiO2 (VII)

The so-called N3 dye, Ru(4,4′−COOH−2,2′−bpy)2(NCS)2, is one of the most well-studied dyes in terms of dye-sensitization of TiO2 due to its efficiency.2 Therefore, this system is a natural choice of system to study with the cluster approach. N3 adsorbed on TiO2 was modeled using the (TiO2)38 cluster with a large anatase (101) surface. The dye was adsorbed in a prototype binding of the two carboxylic acid anchor groups of one of the bpy ligands in a bridging bi-dentate adsorption mode. Due to the multiple attachment sites no attempts of partial or stepwise optimization were performed, instead the whole system was fully optimized at the B3LYP/VDZ level with the LANL2DZ basis set on the N, S, and Ru atoms. The calculation was performed on a single processor machine and required months of CPU time to complete the geometry optimization due to the many structural degrees of freedom of the system. The electronic structure was calculated with an additional function on oxygen (VD(T)Z).

Relaxation of the geometry results in significant strengthening of the bonds between the dye and TiO2, and structural adjustments are seen in both the dye and the nanoparticle. Since the thin nanoparticle model is relatively small for the large N3 dye, distortions are seen in the entire TiO2 framework, and not only at the sites of attachment. The carboxylic groups that are adsorbed on the surface are twisted out of the bpy plane and the overall dye structure is slightly tilted so that one of the NCS groups is located only ca. 3.5 Å above the closest Ti and O neighbor. Experimental evidence for possible interaction of the NCS groups with the TiO2 surface has been reported.111

In the electronic structure of the N3−(TiO2)38 system, no shifts of either dye or TiO2 levels are seen upon connection, as was seen for the charged RuII(tpy)2 dyes. The dye HOMO is located in the center of the band gap and consists of Ru 4d orbital character mixed with NCS ligand χ character. Selected MOs of the dye-sensitized system are shown in Figure 17. The lowest unoccupied dye orbitals are located at the edge of the TiO2 conduction band, resulting in the two lowest levels of the combined system, LUMO(ads) and LUMO+1(ads), being almost entirely of dye orbital character. Hence, the electronic coupling of the lowest dye LUMOs and the TiO2 conduction band is negligible. The following six unoccupied levels in the dye-sensitized system have orbital character almost entirely on the TiO2 part. Subsequently, two dye levels are found to mix with the TiO2: the LUMO+2(ads) which is mainly delocalized on the remote bpy ligand in the dye part, and LUMO+3(ads) which is mainly delocalized on the binding bpy ligand. The calculated electronic coupling is stronger for LUMO+3(ads) because of the spatial orbital overlap of the binding bpy ligands and the TiO2 surface. The resulting injection times are on the order of 10 fs for LUMO+3(ads) and on the order of 100 fs for LUMO+2(ads).
Although the calculated results are not directly comparable with experimental results, considering for instance that it is the dye LUMO level and not the actual excited state that is investigated in the computational approach, the calculated electronic structure agrees overall reasonably well with experimental evidence about the system.\textsuperscript{112} The use of a larger, less reorganized TiO\textsubscript{2} model would decrease the calculated band gap and thus probably mix unoccupied dye and TiO\textsubscript{2} levels so that there would be a stronger electronic coupling between the lowest dye levels and TiO\textsubscript{2}. However, an almost perfect agreement of the different levels as was seen in Section 5.3 should not be expected for this approach.
6 Summary and concluding remarks

In the investigation of geometrical and electronic features for a series of Ru(II)-polypyridyl complexes, certain structural features are shown to affect the electronic structure. For example that the bpy moiety has a bonding contribution in the LUMO that leads to relative stabilization of this orbital, which is lost when a methylene bridge is inserted, leading to loss of absorption of light in the visible region.

The relative energetics of $^3$MLCT and $^3$MC states of four ruthenium complexes have been investigated by explicit identification of equilibrium geometries of such triplet states. This approach provides detailed insight beyond that of the commonly used approach to estimate $^3$MLCT and $^3$MC relative energetics only from vertical excitation energies calculated at the ground state geometry, and can be very useful in the design of new ligands and complexes. This is exemplified by the calculations for the Ru$^{II}$ (pmp)$_2$ chromophore, which predicted several undesirable properties, such as for instance lack of absorption of visible light and high relative energy of the $^3$MLCT excited state compared with the $^3$MC excited state. These excited state energetics are undesirable in terms of photosensitization, because the $^3$MC state leads away from the desired electron transfer process.

It has been reported in several studies that it is important to include solvent effects in the calculations of absorption spectra of ruthenium polypyridyl chromophores. We find that solvent effects estimated using the PCM solvent model do not change the calculated spectra of “pure” ruthenium polypyridyl dyes significantly. However, for the investigation of dyes with nominal net charges and unsaturated spacer or anchor groups, the inclusion of chemical environment is crucial for the description of the electronic and spectral properties. Exclusion or inclusion of chemical environment can even alter the predicted direction of excitation. Furthermore, we demonstrate that inclusion of explicit counter ions can be used to model the chemical environment. We also show how unsaturated spacers can mediate the electron transfer process due to LUMOs that are distributed over both chromophore and spacer, which was not found for the investigated saturated spacers.

The 1-2 nm sized TiO$_2$ clusters, constructed as chemical models of nanocrystalline TiO$_2$ from crystal structure data using DFT, show well-developed band gaps with essentially no band gap states. The two efficient methods used to fully optimize the clusters result in different degree of structural reorganization. The more reorganized structures have larger calculated
band gaps than the less reorganized structures. Detailed knowledge about the advantages and disadvantages with a certain bare nanoparticle model is crucial for the modeling of the dye-sensitized system. For instance, in the highly reorganized models, the larger band gap is a result of unoccupied levels that have been pushed up in energy and occupied levels that have been pushed down. As a result, the level spacing between the lower unoccupied levels is rather small, which is advantageous, however, the energetically high position of the conduction band can result in dye LUMOs located under the band edge. Contrary for the less reorganized structures, low-lying dye LUMOs will likely be located within the conduction band, which however will have a larger spacing leading to an orbital mixing with fewer available levels. Another potential problem in the modeling of TiO$_2$ is that the position of the orbital levels appears to be basis set sensitive, and thus the method for electronic structure calculation has to be carefully chosen.

Modeling of dye–semiconductor interaction is computationally very demanding. We have shown that it is possible to do such modeling using cluster models, and that it is even doable to investigate the lowest excitations. When the conditions for electronic coupling strength controlled electron transfer are fulfilled, it is possible to calculate estimates of electron injection times in qualitative agreement with experimental observations. For perylene-TiO$_2$ systems, we find that the conjugated ethenylene spacer gives five times faster electron injection compared with the saturated ethylene spacer. This calculated relative value compares even quantitatively well to the experimentally observed difference of 5.7 between ethenylene and ethylene spacers for this system.

When studying the charged dye Ru$^{II}$tpy$_2$ adsorbed on a TiO$_2$ cluster it was observed that neutralization of the system with two counter ions was required in order to obtain a well behaved model with realistic interfacial energy level alignment. Injection times in the sub-200 fs regime were estimated for all the investigated Ru$^{II}$tpy$_2$-TiO$_2$ systems, and it was found that the systems with phosphonic acid anchors gave consistently longer injection times than similar systems with carboxylic acid anchors in good agreement with experimental observations.

The use of even larger chemical models than those that are computationally manageable today would be desirable. However, the size of the TiO$_2$ models presented here are large, and therefore only one other DFT study with anatase systems of similar size, which was published this year, can be found in the literature. Pushing the limits of the size of model system even further will be possible in the future as computers become more efficient, and accuracy and availability of low-scaling computational methods increases. However, effects due alone to the size of the molecular model are not expected to be significantly different until the system size is at least doubled.
Summary in Swedish

Kvantkemisk modellering av infärgad titandioxid
Rutenium-polypyridyl- och perylen-färgämnen, titandioxid nanopartiklar och deras gränssnitt


I denna avhandling har kvantkemiska beräkningsmetoder, mer specifikt s.k. täthetsfunktionalteori, som förkortas DFT efter engelskans "density functional theory", använts för att på en atomär och elektronisk nivå modellera färgämnesmolekyler och TiO₂ nanopartiklar. Med hjälp av kvantkemiska beräkningar kan man erhålla detaljerad information om geometri och elektronstruktur, men eftersom beräkningarna är mycket krävande med avseende på datorkraft och datorminne har tidigare studier på infärgad titandioxidid varit begränsade till mycket små TiO₂ modellsystem. Ett övergripande mål med denna avhandling har varit att finna metod- och modellval som möjliggör studier av modellsystem som i storlek nårmar sig realistiska system. Strategier för att uppnå detta har varit val av effektiva basfunktioner, kemiska modeller av TiO₂ med hög koordinering av alla atomer, stegvis geometrioptimering och inkludering av kemisk omgivning i form av få explicita motjonsmolekyler. För att få ökad kunskap och förståelse av systemen samt att utvärdera kvaliteten på de kemiska modellerna och valen av beräkningsmetoder, mer specifikt DFT, har vi använt kvantkemiska beräkningsmetoder för att på en atomär och elektronisk nivå modellera färgämnesmolekyler och TiO₂ nanopartiklar.
ningsmetoder studerades inledningsvis de isolerade färgämnen, därefter näkna TiO\textsubscript{2} partiklar, och till sist infärgade TiO\textsubscript{2} partiklar.

En grupp av rutenium-polypyridylfärgämnen har studerats i detalj i delarbete I och II. Dessa färgämnen är förutom för nanokristallina solceller också mycket viktiga inom forskningsfältet artificiell fotosyntes, som försöker att imitera de inledande processerna i naturlig fotosyntes i gröna växter. Istället för att omvandla solenergi till elektricitet som i solceller, är målet att framställa bränsle i form av vätmång från solljus och vattenmolekyler med hjälp av syntetiskt framställda molekymlägen i vilka solljuset fångas upp av dvs. rutenium-polypyridylfärgämnen. Inledningsvis, i delarbete I, studeras sambandet mellan ligandernas koordineringsgeometri runt ruteniumjonen och den så kallade ligandfältsplittringen samt livslängden på ett exciterat triplettillstånd kallat \textsuperscript{1}MLCT som uppstår genom att en elektron förs från en metallerbital till en energetiskt högre liggande obesatt ligandorbital. Vidare, i delarbete I och II, undersöks för ett antal färgämnen geometrier och relativa energier för \textsuperscript{1}MLCT tillstånd och ett annat exciterat triplettillstånd kallat \textsuperscript{3}MC där en elektron förs från en metallcentrerad orbital till en högre liggande obesatt metallicentrerad orbital. Den relativa energin för dessa två exciterade tillstånd har betydelse för livslängden på \textsuperscript{1}MLCT tillståndet, vilket är viktigt för att den fotoexciterade elektronen ska ha tid att föras vidare från färgämnet. Undersökningarna visade att små förändringar i liganderna kan resultera i stora energiskillnader mellan de exciterade tillstånden.

I delarbete III och IV, undersöks olika förankrings- och mellanrumsgruppers inverkan på färgämnets geometri, elektronstuktur och absorptionspektrum. Resultaten från beräkningarna tyder på att grupper för vilka den lägst obesatta färgämnesorbitalen är delokaliserad på mellanrums- och/eller förankringsgruppen kan assistera elektronöverföring från färgämne till titan-dioxid. I modelleringen av rutenium-polypyridylkomplex med en positiv nettoladdning som innehåller omättade förankrings- och mellanrumsgrupper visade det sig nödvändigt att inkludera den kemiska omgivningen, dvs. i form av s.k. polariserbara lösningsmedelsmodeller eller motjionsmolekyler, för god överensstämmelse med experimentell data.

I delarbete V studeras ett antal kemiska modeller av TiO\textsubscript{2} nanokristaller i storleksordningen 1-2 nanometer, som också används i delarbete IV, VI och VII. Dessa TiO\textsubscript{2}-modeller är laddningsneutrala, stökiometriska och baserade på full geometrioptimering av atomerna i en startstruktur utskuren ur TiO\textsubscript{2} kristallstruktur. På grund av den stora andelen ytatomer resulterar geometrioptimeringen i betydande strukturerelaxering där den genomsnittliga bindningslängden mellan titan och syre atomerna minskar. Studien visar att graden av relaxering beror på val av beräkningsmetod. Då storleken på titan-dioxidsystemet ändras från en enskild molekyl till en nästan oändlig kristall förändras elektronstrukturer från att bestå av enskilda molekylära energinivåer till mycket tätt liggande nivåer som bildar energiband. De kemiska modellerna av TiO\textsubscript{2} kan betraktas som mycket stora molekyler eller små nano-
Kristaller. Den beräknade elektronstrukturen har tätt liggande energinivåer, där de besatta och obesatta nivåerna är separerade av ett bandgap fritt från energinivåer. Då storleken på de kemiska modellerna ökar minskar avståndet i energi mellan närabligande nivåer inom banden. Dessutom minskar bandgapet mellan de besatta och obesatta nivåerna gradvis mot värdet för en nästan oändlig kristall när klusterstorleken ökar.

8 Acknowledgment

I would like to thank my supervisor, assistant supervisor, co-authors, colleagues, friends and family for help and support in the writing of this thesis.
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