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#### COUPLING CHROMOPHORES TO METAL AND SEMICONDUCTOR NANOPARTICLES FOR ENERGY CONVERSION

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"The chemists are a strange class of mortals, impelled by an almost insane impulse to seek their pleasures amid smoke and vapour, soot and flame, poisons and poverty; yet among all these evils I seem to live so sweetly that may I die if I were to change places with the Persian king." Johann Joachim Becher (1635-1682)

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## Preface

The object of this thesis is the development of hybrid organic-inorganic systems based on molecular species and nanoparticles, to perform complex photophysical functions, with possible applications in the field of solar energy conversion.

Chapter 1 Introduces the basic properties of solid state materials and semiconductor nanoparticles, together with the principles guiding the development of artificial photosynthetic systems. Examples from literature will be presented, with special emphasis on the emerging role of nanoparticles in the field.

Chapter 2 Describes an organic-inorganic antenna system based on a silicon nanoparticle and a conjugate oligomer, focusing on the photophysical processes occurring upon one-photon and two-photon excitation.

Chapter 3 Illustrates the synthesis and photophysical properties of a family of red-NIR luminescent zinc complexes designed for the realization of organic-inorganic hybrids with silicon nanoparticles, with a focus on a serendipitous chemical transformation leading to a novel class of fluorescent complexes.

Chapter 4 Presents the synthesis and hydrogen evolving activity of a supramolecular system composed of a photoactive dendrimer and a platinum nanoparticle, a novel approach in the field of artificial photosynthesis.

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# Chapter 1

## Introduction

This thesis work will describe some experimental studies in which molecular species have been coupled to nanoparticles (or have been designed to do so) to realize hybrid systems capable of performing complex photophysical functions. In particular, we will make use of semiconductor quantum dots and metal nanoparticles, with the goal to integrate such materials in artificial photosynthetic processes that have been traditionally performed by molecular systems.

This approach combines the advantages of the very precise, relatively easily predictable and theoretically well described properties of simple molecules with the much less understood intriguing properties arising from materials on the nanoscale.

Nanomaterials have been extensively studied only in recent years because, oversimplifying, they are too little for the solid state physicist and too big for the molecular chemist. This is however, also the main reason why they attracted so much interest, since they constitute a "bridge" between disciplines and contribute to give a unified description of phenomena such as optical or electrical properties over a dimensional scale that goes from the single atom to the bulk material<sup>1</sup>.

This can be done following two possible pathways, starting from the molecule (or the atom) and building bigger and bigger systems, from aggregates or cluster of atoms to nanoparticles (and all the other possible types of nanomaterials) or starting from the bulk solid and shrinking the size more and more, until classical physics becomes an insufficient description and quantum effects arise, modifying the properties of a material to the point of making it completely different from itself on the macroscopic scale.

Inevitably, this leads to the necessity of dialogue between disciplines that have their own language and way of approaching a problem, a task that is far from being simple.

To introduce the field, we will first of all give a brief and "as chemical as possible" description of solid state physics, mainly to elucidate the language and notations that

<sup>&</sup>lt;sup>1</sup>Scholes, G. D. et al. (2006). Nature materials 5, 683–696.

will be useful to understand a subject that has been extensively used to describe the properties of nanomaterials, but that may result quite obscure to the molecular chemist, without any purpose of an accurate description.

We will then illustrate briefly the effect of the nanoscale on solid materials, focusing on semiconductor quantum dots and in particular on silicon ones.

Finally, we will describe the field of artificial photosynthesis, one of the possible approaches to solar energy conversion, with particular emphasis on the increasing role of nanomaterials for performing the photoredox processes involved. A special focus will be put on the integration of silicon and platinum nanoparticles (the two types of materials used in this work) in hybrid organic-inorganic systems for light absorption, charge separation and catalysis of fuel generating reactions.

This thesis work was developed in the framework of the ERC Project "PhotoSi", funded by the European Union.

#### 1.1 A few notions of solid state physics

The properties of solid state materials, and in particular the optical properties, are determined by their electronic structure. Contrarily to molecules, which have discrete electronic levels, in solids this levels are so many and so little separated in energy that it is more useful to describe the electronic structure as composed of bands. Since this is the type of materials we will work with, we will implicitly refer to crystalline solid materials, in which atoms are disposed in a precise regular lattice. Two approaches can be used to explain their band structure:

- Describe the electrons as free particles in vacuum and then modify their wavefunction applying a periodical potential generated by the periodical lattice,
- Start from the orbitals of the atoms composing the lattice and combining them to form the bands.

We will follow this second approach, to start from the point of view of the molecular chemist<sup>2</sup>, and finally integrate it with the free particle model to illustrate some concepts that are better understandable from the point of view of the solid state physicist.

For simplicity, we will model our crystal lattice in only one dimension. The three dimensional case is obviously more complicated, but the conceptual description is exactly the same. As a first, very simple model, we choose a linear chain of equally spaced hydrogen atoms.

<sup>&</sup>lt;sup>2</sup>Hoffmann, R. (1987). Angewandte Chemie International Edition in English 26, 846–878.

-0-0-0-0-0-

Figure 1.1: An ideal chain of equally spaced hydrogen atoms (Reprinted with permission form ref (2)).

When considering a crystal lattice of a bulk material, the number of atoms composing it is so big that normally is defined as "infinite". This doesn't take into consideration the fact that surface atoms are different from bulk ones, but their contribution with respect to the total number of atoms is so little that they can be safely ignored. A convenient way to do that is to think of our chain as an imperceptibly bent segment of a very large ring of atoms ("cyclic boundary conditions").

This assumption allows to consider how the orbital structure changes as, starting from a simple couple of atoms, the number of atoms is increased, forming progressively larger rings, as shown in *Figure 1.2*.



Figure 1.2: The orbital diagrams of circular structures composed of a progressively increasing number of atoms. (Reprinted with permission form ref (2)).

It is clear that progressively increasing the number of atoms, the levels become less separated in energy and start to assume the form of a band. In particular, they are composed of couples of degenerate orbitals, with only the lowest level (corresponding to the most "bonding" configuration) and the highest (corresponding to the most "antibonding" one) that are non-degenerate. The levels are not equally spaced, but their density is maximal at the top and bottom of the band.

Considering again the linear structure shown in *Figure 1.1*, assigning positive integers numbers to each atom (n = 0,1,2,3,4...), defining  $\chi$  the function corresponding to the 1s orbital of each atom ( $\chi_0, \chi_1, \chi_2, \chi_3, \chi_4$ ...) and *a* the distance between a couple of nearest neighbour atoms, it is possible to write the symmetry adapted (translation is a symmetry operation) wavefunctions of the system as:

$$\psi_k = \sum_n e^{ikna} \chi_n \tag{1.1}$$

where k is an index for the irreducible representation of the wavefunction. We will see that k is much more than that, but for the moment it is sufficient to say that each of the levels shown in *Figure 1.2* has its own k value and  $\psi_k$  wavefunction. Let's take two definite values of k, k = 0 and  $k = \pi/a$ . If we substitute k in equation 1.1, we obtain the wavefunctions for the lowest and highest orbitals shown in *Figure 1.3*:

Figure 1.3: The wavefunctions resulting from the cases k = 0 and  $k = \pi/a$ . (Reprinted with permission form ref (2)).

The value k can be also considered as a "node counter": the higher is the value of k, the larger is the number of nodes in the wavefunction. It can be demonstrated that for values of  $k > \pi/a$ , the obtained functions are just a repetition of some function already obtained for other k values. The range of unique values for k is  $-\pi/a \leq k \leq \pi/a$ , and this is called the "first Brillouin zone". Since it can be easily proven that E(k) = E(-k), it is possible to describe the electronic properties in the restricted interval  $0 \leq k \leq \pi/a$ .

Also, the values of k are equally spaced in the space of k, which is called "reciprocal or momentum space". This name comes from the fact that  $k = 1/\lambda$  is also the wavevector of the electron in the state  $\psi_k$  and it is directly proportional to the electron momentum through the de Broglie relationship  $\lambda = h/p$ .

By plotting the energy of the level  $\psi_k$  versus k, it is possible to obtain the band structure of the system (*Figure 1.4(a)*). It can be seen that the slope of the curve is maximal near the central values of k, where the orbitals are more spaced in energy, and that it has its minimum for the most bonding configuration (k = 0) and its maximum for the most antibonding one ( $k = \pi/a$ ).

The shape of the band depends on the type of interacting orbitals. In the case of p orbitals for example, the most bonding configuration corresponds to  $k = \pi/a$  and the most antibonding one to k = 0 and the band shape is inverted with respect to the previous case (*Figure 1.4(b)*).

When considering a more complex system than the simple hydrogen atom, one has to take into consideration all the atomic or molecular orbitals of the repeated unit. To give an idea of what a real band diagram looks like, it is possible to choose the ideal



Figure 1.4: (a) The band structure generated plotting the energy in momentum space for a linear chain of s orbitals. (b) The band structure obtained in the case of p orbitals (Images reprinted and adapted with permission form ref (2)).

system composed by a chain of  $[PtH_4]^{2-}$  complexes connected through Pt-Pt interactions, and look how the molecular orbitals of the Pt complex combine to generate the bands. Here another important concept that emerges is that not all bands have the same width in energy, but the bands corresponding to orbitals oriented along the axis connecting the Pt atoms, forming  $\sigma$  bonds and thus having the highest degree of overlap, generate larger bands, followed in order by the ones forming  $\pi$  and  $\delta$  bonds (*Figure 1.5(a)*).



Figure 1.5: (a) A schematic representation of the bands generated by the interaction of the different molecular orbitals of  $[PtH_4]^{2-}$ , featuring a width that is proportional to the degree of overlap. (b) The band diagram generated by the same complex and the corresponding density of states. (Images reprinted with permission form ref (2)).

The corresponding band diagram looks more complicated, presenting a combination of band shapes and widths that lead to crossing between different bands. A convenient way to describe the distribution of the levels is to plot the so-called "density of states" diagram (DOS), which shows the total number of levels at each energy value (*Figure* 1.5(b)).

The filling of the bands with electrons is very simple and is analogous to the filling of molecular orbitals upon combination of atomic orbitals. All the bands that are generated from orbitals containing two electrons will be completely filled, the bands generated from orbitals containing one electron will be half-filled and the bands generated from empty orbitals will be empty.

This leads to the definition of the analogues of the HOMO and LUMO levels in molecules. The highest energy band filled with electrons is defined as "valence band" and the lowest energy empty band is defined as "conduction band". Like in molecules the HOMO and LUMO (the frontier orbitals) define most of the properties of the molecule, such as the chemical reactivity, the redox potentials and in many cases the photophysical properties, the valence and conduction bands control the electronic properties of the material.



Figure 1.6: The position of valence and conduction bands for metals, semiconductors and insulators.

The energy gap between the valence and conduction bands defines the conductance properties of a solid. When the two bands are superimposed in energy, there is no band gap and the solid is a metal (another case would be a semi-filled valence or conduction band, even in presence of a large band gap). When the band gap is very large we are in presence of an insulator, while the intermediate case is that of semiconductors (band gap in the order of few eV). The peculiarity of semiconductors is that due to the effect of thermal energy, some electrons can pass from the valence to the conduction band, and thus improve the conductance of the material (the same material can behave as an insulator at a given temperature and as a semiconductor at another, higher, temperature). The "Fermi level" is defined as the hypothetical level (in semiconductors for example, it is in the middle of the band gap, where there is no real level) in which there is the 50% probability of finding an electron (at a given temperature). Another useful concept to describe the physics of solid state materials is that of "quasi-particle", that derives from the solid state physics approach to the problem. As said above, using this treatment the simple case of a free particle is firstly considered. This is the simplest problem in quantum mechanics and has the following solutions for its wavefunction (considering only the spatial coordinate r) and energy:

$$\psi_r = A e^{ikx}$$

$$E = \frac{k^2 \hbar^2}{2m}$$
(1.2)

where A is the amplitude of the wave, and m is the mass of the particle. The case of a particle in a solid material is of course much more complicate, due to the electrostatic effects of the lattice and of the electron cloud, giving rise to a very large number of interactions that make the Schrödinger equation of the system definitely unsolvable. However, it has been found that, very conveniently, it is possible to describe a particle in a solid just as a free particle, but with a different mass, the so called "effective mass". This is the core of the concept of quasiparticle.

In solid state physics, the most important quasi-particles are:

- *The electron*, also defined as "electron in solid", since its mass is not the electron mass, but the apparent mass of the electron under the influence of the ensemble of the other particles of the solid.
- *The hole*, is the reverse of the electron, i.e. the ensemble of all the electrons of the solid under the influence of the "missing" of one electron.
- *The exciton*, is an overall neutral quasiparticle composed of an electron-hole pair. It can be generated for example by absorption of a photon and it's the quasi-particle involved in the optical transitions.
- *The phonon*, is a collective movement of the nuclei in the solid, and can be roughly considered as an analogous of a vibrational mode in a molecule.

Given this premises, it is possible now to consider the optical properties of semiconductor materials. In semiconductors, a photon with a suitable energy can promote an electron from the valence to the conduction band, creating an exciton. In the reverse process, the recombination of the exciton can generate a photon, giving rise to luminescence.

There is an important difference among semiconductors in this regard, and two classes can be defined:

- Direct band gap semiconductors, in which the maximum of the valence band and the minimum of the conduction band are located at the same k value.
- Indirect band gap semiconductors, in which the maximum of the valence band and the minimum of the conduction band are located at different k values.

This has a profound influence on the photophysical properties (*Figure 1.7*). Given the fact that the momentum of the photon is infinitesimally small and that momentum conservation is a requirement for the transition to occur, the absorption of a photon would be much favoured in direct band gap materials, while in the indirect case it is required the assistance of a phonon (a concept conceptually similar to vibronic coupling in molecules). The same is valid for the luminescence. These concepts will be better illustrated in the next chapters when comparing direct band gap quantum dots with the indirect band gap silicon case.



Figure 1.7: A schematic representation of the band maxima and minima positions in direct and indirect band gap semiconductors and the implication on photon emission (Reprinted with permission form ref (3)).

The band structures shown in the above discussion were very conveniently derived in the case of a mono-dimensional chain of atoms, with k values easily represented as an equally spaced series in the interval  $0 \le k \le \pi/a$ . Things get more complicated when considering a real 3D crystal.

To deal with the problem, the type of crystal lattice of the specific material whose bands need to be described should be taken in consideration. The discussion of the various crystalline structures and Bravais lattices that can be encountered in solid state materials is out of the scope of this discussion and we will simply choose the face centered cubic (fcc) structure, that is common to most of the materials of interest in this discussion (among which silicon and platinum). It can be composed of just one type of atoms, like in silicon, or two different types, like in ZnS (from which it takes also the name of "zinc blende" structure). It is mathematically possible to take a lattice in its real-space physical structure (also called "direct lattice") and translate it through Fourier transform in momentum space (or "reciprocal space", realising the so-called "reciprocal lattice"). The elementary cell of the reciprocal lattice (using a particular type of cell, called Wigner-Seitz cell) is called "first Brillouin zone", exactly the same concept that has been exposed above to draw the band structures in one dimension.



Figure 1.8: (a) Above: the Weigner-Seitz cells for the direct (left) and reciprocal (right) lattices of a fcc structure. Below: the first Brillouin zone of a fcc lattice with indexes indicating special points on its surface. (b) The band diagram for Si (indirect band gap) and GaAs (direct band gap) as calculated in ref (4).

Looking at Figure 1.8(a), the central point of the cell is indicated as  $\Gamma$ , while a series of special points (angles, centers of edges or faces) are drawn and indexed with Roman letters. The directions connecting the central point  $\Gamma$  to some of the special points are indicated with Greek letters. The same indexes are reported in the band diagrams of Figure 1.8(b) for Si and GaAs (only Roman letters are reported in these diagrams, sometimes Greek letters are present between points to indicate the direction, but they are optional) and allow to understand what happens to the band structure while following the direction connecting i.e.  $\Gamma$  to X, or W to K etc. This diagram is an useful tool to draw on the paper a three-dimensional band structure and allows to immediately understand if the material is a direct band gap (like GaAs) or indirect band gap (like Si) semiconductor.

After this short introduction on the electronic properties of bulk solids, in the next sections we will describe what happens when dimensions are reduced to the nanoscale, with special attention to semiconductor materials.

#### 1.2 Solids at the nanoscale

The reduction of the dimensions of a solid to the few nanometer scale gives rise to different classes of materials: if just one dimension is nanometric (forming a sort of flat sheet) 2D quantum wells are produced, if two dimensions are reduced 1D quantum wires are formed and finally if all the three dimensions are in the nanometer range, 0D quantum dots are obtained. We will focus our attention on this last class of materials.

Two main effects are important to define the properties of nanomaterials:

- The increase of the surface to volume ratio. Considering a spherical material and counting the atoms on the surface and those in the bulk of the sphere, for a macroscopic material the number of superficial sites is negligible with respect to the bulk sites, while when shrinking the size to the few nanometers scale, the ratio increases enormously, with great advantage to surface dependent applications such as heterogeneous catalysis. This however implies that surface effects are no more negligible when evaluating the electronic and optical properties and can even dominate them.
- Quantum confinement. An exciton in a bulk material can be more or less delocalized, i.e. it has a finite size, defined by the exciton Bohr radius  $(a_b, \text{typical} dimensions in the range 1-100 nm)$ . When the dimensions of a nanocrystal are reduced to a size comparable with  $a_b$  (the "quantum confinement regime"), the optical and electronic properties are dependent on the size (this is particularly evident for light absorption and luminescence).

The effect of quantum confinement leads to a discretization of the levels with respect to the solid (by reducing both the number and density of the levels), as particularly evident at the band edges of semiconductors. For this reason, nanocrystals can be considered a sort of "intermediate" between molecules, in which the charges are very localized, giving rise to very well separated levels, and solids, in which the charge is delocalized over a large spatial region, giving rise to bands.

It should be noted that this effect affects metals as well, but, since their bands are overlapping, even when increasing discretization the structure is still substantially a band and no discrete absorption or emission peaks are observed, unless dimensions are reduced to the point of obtaining small clusters composed of a few tenths of  $atoms^{6-8}$ (*Figure 1.8(b)*). A different phenomenon arising in metal nanoparticles is that of plasmon

<sup>&</sup>lt;sup>6</sup>Zhang, L. et al. (2014). Nano Today 9, 132–157.

<sup>&</sup>lt;sup>7</sup>Sun, H.-T. et al. (2013). Science and Technology of Advanced Materials 15, 014205.

<sup>&</sup>lt;sup>8</sup>Díez, I. et al. (2011). Nanoscale 3, 1963–1970.



Figure 1.9: (a) Energy levels in molecules, semiconductor nanocrystals and bulk semiconductors (Reprinted with permission form ref (5)). (b) Energy levels in metal from the atom to the bulk scale (Reprinted with permission form ref (6)).

resonance, a collective oscillation of the electron cloud of the particle upon interaction with the electrical field of light. A few examples will be given in the following sections, but its description is out of the scope of this work.

In the framework of the effective mass approximation (EMA), that assumes that the effective masses of the electron and hole in the nanocrystal are the same as in the bulk solid, quantum confinement can be roughly divided in two regimes<sup>9</sup>:

- *Weak confinement.* The radius of the particle is still considerably bigger than the exciton Bohr radius, and the system can be modelled as an exciton in a spherical potential (analogous to an hydrogen atom in a spherical potential).
- *Strong confinement.* The radius of the particle is considerably smaller than the exciton Bohr radius, and the system can be considered as an electron and a hole, in a first approximation non-interacting, inside a spherical potential.

In the latter regime, a strong effect on the band gap energy, that increases progressively with the reduction of the size of the nanocrystal is responsible for the intriguing features that arise both in absorption and in emission. These properties are dependent on the direct or indirect nature of the band gap. In this section we will speak about direct band gap semiconductors to introduce the level structure, selection rules and surface effects, while the specific features of indirect band gap semiconductors will be treated in the next section for silicon quantum dots.

Considering the case of strong confinement, one can first model the system neglecting the Coulomb interaction between electron and hole and assuming as infinite the potential outside the sphere, and as 0 its value inside the boundaries (particle in a spherical box).

<sup>&</sup>lt;sup>9</sup>Gaponenko, S. V., Optical properties of semiconductor nanocrystals, 1998; Vol. 23.



Figure 1.10: (a) Energy levels in quantum dots using the model of non-interacting electron and hole in an infinite spherical potential (Reprinted and adapted with permission form ref (9)). (b) Absorption (above) and emission (below) spectra of CdSe QDs of different size (Reprinted with permission form ref (5)).

This gives rise to two independent series of levels, one for the electron and one for the hole, defined by two quantum numbers n and l, of the type 1s, 1p, 1d etc. The subscript "e" indicates the electron levels (1s<sub>e</sub>, 1p<sub>e</sub>, 1d<sub>e</sub>...), while the subscript "h" indicates the hole levels (1s<sub>h</sub>, 1p<sub>h</sub>, 1d<sub>h</sub>...). Selection rules allow transitions between levels with the same quantum numbers ( $\Delta n = 0$ ,  $\Delta l = 0$ ). This is an oversimplified approach that doesn't take into account for example the coulomb interaction between the electron and hole, the finite nature of the barrier, the surface polarization and spin-orbit coupling effects<sup>9,10</sup>, but it can be used to qualitatively describe the origin of the optical properties shown in *Figure 1.10(b)*.

Direct band gap semiconductors, such as CdSe shown in Figure 1.10(b), show an absorption spectrum characterized by a low energy excitonic band with molar absorption coefficients in the order of  $10^5$  cm<sup>-1</sup> M<sup>-1</sup> (corresponding to the  $1s_h \rightarrow 1s_e$ transition) and then a progressively increasing transition probability going towards the UV, corresponding to transitions between levels that are located in regions of progressively increasing density of states (the separation of the levels is higher near the band gap), forming a continuum in the spectrum.

In emission, they show an intense luminescence band  $(1s_e \rightarrow 1s_h \text{ transition})$  with a very narrow profile, as compared to the emission bands of molecules. As will be shown

<sup>&</sup>lt;sup>10</sup>Nozik, A. J. (2001). Annual review of physical chemistry 52, 193–231.

more in detail for silicon in next section, the band width of QDs should be even more narrow, but there is a widening effect due to the size distribution of the particles in the ensemble in solution used to record the spectra.

An important role on the photophysical properties of quantum dots is played by surface, as illustrated in *Figure 1.11* for CdSe QDs. The atoms on the surface are incompletely bonded, i.e. they have a dangling orbital pointing towards the external environment. These orbitals are highly ordered and can form bands that, if they fall inside the band gap, can quench the exciton emission and/or give rise to other luminescence processes. This is especially the case of Se<sup>2-</sup> atoms, presenting a filled dangling bond, that can generate traps for the hole quasiparticle (*Figure 1.11*). On the contrary, the empty orbitals of Cd<sup>2+</sup> are passivated in solution by appropriate ligands (e.g. TOPO, trioctyl phosphine oxide, that has also the role to increase the solubility of the particle) and their band gap emission is preserved. An inherent source of instability in QDs is the possibility of a chemical reaction with some species in the environment that removes (or adds) an atom from the lattice, creating a charge inhomogeneity that can act as a trap.



Figure 1.11: A schematic representation of the surface dangling bonds for CdSe QDs with excess of cations or anions and the effect on the band structure and emission properties (Reprinted with permission form ref (5)).

A strategy frequently used to stabilize the emission of QDs is to coat them with a layer of a second semiconductor with a larger band gap (es. CdSe/ZnS), realizing a core-shell architecture, that has the multiple role of passivating the surface of the core,

isolate it from the external environment and confine the exciton far from the surface, resulting in a brightly emissive and very stable material.

#### 1.3 Silicon nanoparticles

In the field of semiconductor quantum dots, a particular role is played by silicon nanoparticles. Despite the fact that they exhibit luminescent properties arising from quantum confinement, they have important differences with respect to direct band gap quantum dots:

- *Indirect band gap.* The indirect band gap electronic structure of silicon is retained when shrinking the size of the crystal to nanometric dimensions. This has a profound influence on the photophysical properties, particularly on the absorption spectrum and exciton lifetime.
- Surface derivatization. At least up to now, the main strategy used to control the luminescence of direct band gap QDs, the creation of a core-shell structure, has been limited to the creation of a silica layer by oxidation of the silicon nanoparticle. However, a very rich radical chemistry on the silicon surface allows for the formation of covalent bonds, particularly Si-C bond, suitable for integration of SiNPs with organic materials. Due to the high reactivity of the surface, the formation of defects is likely in many cases and can dominate the photophysics of the material.
- *Greener material.* Silicon is abundant, low cost and non-toxic. Moreover, the silicon industry is by far the most developed in the field of semiconductors.

The understanding of the properties of silicon nanoparticles has traditionally been complicate, with different preparation methods leading to nanocrystals showing strikingly different photophysical properties, originating from band-gap or defect states, with results and interpretations that sometimes were in contradiction and specific arguments that have been highly debated.

Here we will try to give a short discussion on the findings made by researchers in this highly active and still evolving field, following a specific pathway. We will start with a short overview of the synthetic methods to prepare SiNPs, then we will discuss the photophysical properties of alkyl capped SiNCs and use them as a reference to describe the effects of defects and different surface chemistry. Practical applications of silicon nanoparticles have been demonstrated in several fields<sup>11</sup>, such as luminescent polymers,

<sup>&</sup>lt;sup>11</sup>Dasog, M. et al. (2016). Angewandte Chemie International Edition 55, 2322–2339.

cellular imaging, explosive sensing, OLEDs and solar cells, but their description is out of the scope of this work.

#### 1.3.1 Synthesis of silicon nanoparticles

The synthetic methods for the preparation of silicon quantum dots have been presented in different reviews<sup>11-13</sup>. Here we will give a short overview and then describe more accurately the specific method used to prepare our samples.



Figure 1.12: (a) A scheme of the different preparation methods of SiNPs. (Reprinted with permission form ref (13)). (b) A conjugated light harvesting dendron (Reprinted with permission form ref. (11)).

The two main approaches are the so called "top-down" and "bottom-up" routes. In the former, the starting material is a bulk silicon wafer that is either mechanically crushed and then chemically etched or electrochemically etched and sonicated to produce a dispersion of H-terminated SiNPs. The electrochemical method allows to control the dimension of the particles, and thus their emission wavelength, through the tuning of the applied current density and might be promising due to its easy implementation.

The "bottom-up" approach consists in a range of chemical reactions and physical processes applied on a molecular precursor. It has the advantage of using standard chemical lab technologies and to potentially provide a large amount of material with a relatively easy scale-up. Typical examples (*Figure 1.12(b)*) are the oxidation of metal silicides, the reduction of silicon halides or the plasma/laser pyrolysis of silanes.

<sup>&</sup>lt;sup>12</sup>Cheng, X. et al. (2014). Chemical Society Reviews 43, 2680–2700.

<sup>&</sup>lt;sup>13</sup>Dohnalová, K. et al. (2014). Journal of Physics: Condensed Matter 26, 173201.

The method we use, the thermal disproportionation of silicon-rich oxides, belongs to this class and has been developed by Hessel in the laboratory of Prof. Veinot<sup>4</sup> and later expanded in the group of Prof. Korgel<sup>15</sup>.



Figure 1.13: HR-TEM images of SiNPs annealed at different temperatures and a scheme of the synthetic procedure (Reprinted with permission form ref (15)).

In a typical procedure, the molecular precursor hydrogen silsequioxane (HSQ) is put in a quartz crucible and heated in a high temperature furnace under reducing atmosphere (N<sub>2</sub>/H<sub>2</sub> 95:5) at a rate of 20 °C/min until reaching the desired annealing temperature. The sample is kept at this temperature for 1 h and then allowed to cool to RT. The obtained powder is then finely ground and etched with an HF/HCl mixture to remove the surrounding silica matrix and liberate the silicon nanocrystals. After a series of centrifugations with H<sub>2</sub>O and EtOH to remove the etching solution, the nanocrystals are dispersed in dodecene and heated at high temperature to obtain alkyl passivated SiNPs, successively purified by centrifugation with a solvent/antisolvent mixture to yield a pure SiNP powder that is soluble in apolar organic solvents.

The annealing temperature and time can be varied to control the nanoparticle diameter and crystallinity. From FTIR and XPS analysis, the final alkyl passivated surface results to be composed mainly of Si-C bonds, with the presence of Si-O-Si bonds and other Si-O species resulting from oxidations in water and EtOH in presence of

<sup>&</sup>lt;sup>14</sup>Hessel, C. M. et al. (2006). Chemistry of materials 18, 6139–6146.

<sup>&</sup>lt;sup>15</sup>Hessel, C. M. et al. (2011). *Chemistry of Materials* 24, 393–401.



Figure 1.14: (a) The effect of water and oxygen on the Si-H surface groups of SiNPs (Reprinted with permission form ref (16)). (b) The effect of EtOH and oxygen on the Si-H surface groups of SiNPs (Reprinted with permission form ref (17)).

oxygen during the purification process<sup>16,17</sup>. It has been reported for porous silicon, a material that presents several analogies with silicon nanoparticles, that the presence of oxygen traps on the surface should introduce states that are outside the gap (i.e. above the conduction band and below the valence band) at least for diameters bigger than 3 nm<sup>18</sup>. However the influence of oxygen defects has been debated, as shown in the next section.

#### 1.3.2 Photophysics of alkyl passivated SiNCs

Alkyl passivated silicon nanocrystals prepared as described above show absorption and luminescence properties that are dependent on the fact that they are indirect band-gap semiconductors. This is evident from the absorption shapes (*Figure 1.15(a*)), that are typical of indirect band-gaps, lacking the presence of excitonic bands, but progressively increasing towards the UV. While the spectral shape remains very similar, the absorption coefficient progressively increases with increasing dimensions<sup>15</sup>. The indicrect nature of the band gap is confirmed by theoretical calculations at the DFT level (*Figure 1.15(b*)) on small silicon nanoparticles (1.5 to 2.5 nm)<sup>19</sup>.

The luminescence properties of silicon nanoparticles have triggered an active debate, since emission colors from blue to the NIR and emission lifetimes from the nanosecond to the nearly millisecond regime have been observed, usually depending on the different synthetic methods. As a first consideration, this shows without any doubt the huge

<sup>&</sup>lt;sup>16</sup>Mastronardi, M. L. et al. (2014). The Journal of Physical Chemistry C 119, 826–834.

<sup>&</sup>lt;sup>17</sup>Lockwood, R. et al. (2014). *Chemistry of Materials 26*, 5467–5474.

<sup>&</sup>lt;sup>18</sup>Wolkin, M. et al. (1999). *Physical Review Letters 82*, 197.

<sup>&</sup>lt;sup>19</sup>Hapala, P. et al. (2013). *Physical Review B* 87, 195420.



Figure 1.15: (a) Absorption spectra of silicon nanoparticles of different dimensions (Reprinted with permission form ref (15)). (b) Theoretical calculations for 2.5 nm SiNPs coated with different surface groups. The density of states reproduces the typical distribution of indirect band-gap semiconductors. (Reprinted with permission form ref (19)).

importance of surface in controlling the emission properties of SiNPs, as discussed more deeply in the next section.

Alkyl capped nanoparticles prepared with the thermal disproportionation treatment present size tunable luminescence in the red-NIR interval, with a size dependence that seems to be in accordance with theoretical predictions<sup>15</sup> (*Figure 1.16(a)*) and with band gaps measured by scanning tunneling spectroscopy (SLS)<sup>20</sup>, a very valuable tool for this kind of materials since it is able to directly measure the electronic structure at the single nanocrystal level.

With respect to direct band-gap QDs like CdSe/ZnS core shell systems, the spectral width of the emission band is much larger. The reason for this behaviour has been demonstrated using single-dot spectroscopy at room temperature and at 10 K<sup>21</sup>(*Figure 1.16(b)*). Moreover, the effect of a different environment (alkyl layer, SiO<sub>2</sub> matrix or thin SiO<sub>2</sub> layer) has been investigated. The study has clearly revealed ultranarrow luminescent bands at 10 K, with a linewidth < 200  $\mu$ eV (this was the instrumental limit) for all samples. The linewidth at room temperature has a strong dependence on the environment, with a value of 25 meV for Si/thin layer, 90 meV for Si/SiO<sub>2</sub> and 220 meV for Si/alkyl. This enlargement is due to "homogeneous broadening", the effect of temperature that enhances vibrations in the nanoparticle, resulting in a distribution of slightly different structures at the moment of the relatively instantaneous

<sup>&</sup>lt;sup>20</sup>Wolf, O. et al. (2013). Nano letters 13, 2516–2521.

<sup>&</sup>lt;sup>21</sup>Sychugov, I. et al. (2014). ACS Photonics 1, 998–1005.



Figure 1.16: (a) Excitation and emission spectra of silicon nanoparticles of different dimensions (Reprinted with permission form ref (15)). (b) Emission spectra of ensembles of alkyl capped (green) and porous silicon nanoparticles (blue), together with single particles in SiO<sub>2</sub> matrix (red) and thin SiO<sub>2</sub> layer (black) (Reprinted with permission form ref (21)).

photon emission. This demonstrates the possibility of using SiNPs in applications in which narrow emission spectra are beneficial, such as multicolor imaging. However this would require advancements in the synthesis and/or purification procedures, since the remaining large enlargement of the band observed for bulk solutions is due to "inhomogeneous broadening", the effect of the size distribution of the particles.

It is possible to narrow this size distribution through separation methods. In a recent study<sup>22</sup>, an ensemble of alkyl capped SiNPs was separated through ultracentrifugation on a polymer matrix, obtaining a series of fractions whose photophysical properties were progressively changing as result of the progressively increasing size of the particles. This has unequivocally proven that the quantum yield and lifetimes increase with size, while the band maximum progressively shifts to longer wavelengths, demonstrating that non-radiative recombinations progressively dominate with decreasing size. Quantum yields as high as 43% were reported in this study (and up to 60% in another<sup>23</sup>), while lifetimes were found to be in the microsecond range.

The origin of this very long lifetime has been attributed to the effect of oxygen on the surface, as demonstrated in a study in which organically capped green emissive

<sup>&</sup>lt;sup>22</sup>Mastronardi, M. L. et al. (2011). Nano letters 12, 337–342.

<sup>&</sup>lt;sup>23</sup>Jurbergs, D. et al. (2006). Applied Physics Letters 88, 3116.



Figure 1.17: Emission spectra (a) and lifetimes (b) of 2.2 nm SiNPs with progressive amounts of oxidation, together with a scheme showing the hypothesized origin of the two types of emission (Reprinted with permission form ref (24)).

nanoparticles were progressively oxidized, showing the appearance of a new band and an abrupt change in the emission lifetime, passing from the nanosecond to the microsecond regime<sup>24</sup>. The dependence of the emission maximum on the particle size was found to be in accordance with theoretical models for both the green emissive carbon capped species and the red emissive oxidized ones (see also *Figure 1.15(b)*, in which the band gap for oxygen capped SiNPs is narrower with respect to carbon terminated particles of the same size). The fast decaying green emission was assigned to core centered excitons, while the slow decaying red one was hypothesized to be due to surface localized states.

However, in a different study<sup>25</sup>, a nearly opposite behaviour was observed, with "perfectly" alkyl capped (no Si-O peak observed in FTIR) red-emissive SiNPs featuring a lifetime in the microsecond range (attributed to band-gap transitions) and partially oxidized ones showing nanosecond lifetimes and a slightly blue-shifted emission (still in the red region). This illustrates well that the real origin of the long-lived red emission in alkyl capped SiNPs is still unclear and object of active debate.

#### **1.3.3** Effect of surface functionalization

The effect of different surface groups on the photophysical properties of SiNPs has been largely investigated, mainly by the group of Veinot. Beside of the above mentioned effect

<sup>&</sup>lt;sup>24</sup>Dohnalová, K. et al. (2013). Light: science & applications 2, e47.

<sup>&</sup>lt;sup>25</sup>Dasog, M. et al. (2014). ACS nano 8, 9636–9648.



of oxidation on alkyl capped SiNPs emission, in the same study<sup>25</sup> and in others<sup>26,27</sup> several surface groups were introduced, as schematically shown in *Figure 1.18*.

Figure 1.18: Schematic representation of the different emission colors obtained starting from hydrogen terminated (a, reprinted with permission form ref (11)) and halogen terminated (b, reprinted and adapted with permission form ref (27)).

The combined evidences from these studies give a good overview of the surface chemistry resulting from different functionalization approaches and on their effect on photophysics. In particular, all samples except the "perfectly" alkyl terminated (obtained from hydrosylilation of H-terminated particles with alkenes or from reaction of Br-terminated ones with Grignard reagents) and the mixed alkyl/hydrogen terminated SiNPs (obtained from reaction of H-terminated particles with organolithium reagents) displayed nanosecond lifetimes and their emission was attributed to surface-related states. Interestingly, their emission quantum yield was usually higher than that reported for their analogues featuring long-lived red emission.

The effect of oxygen related surface traps is clearly seen from the reaction with  $CO_2$  and from the emission of particles derived from Cl and I-terminated surfaces, with blue and green emissions reported. A similar effect was observed upon reaction of H-terminated SiNPs with amines, that lead to the formation of a mixed oxide-nitride surface and whose color can be tuned from blue to orange depending on the reacting

<sup>&</sup>lt;sup>26</sup>Höhlein, I. et al. (2015). Chemistry-A European Journal 21, 2755–2758.

<sup>&</sup>lt;sup>27</sup>Dasog, M. et al. (2015). Chemistry of Materials 27, 1153–1156.

amine<sup>28</sup>. A particular behaviour was observed upon addition of phosphine oxides, which are able to oxidize the SiNP surface in a controlled fashion, with the emission color changing from yellow to green over time to completely disappear after months of storage. Moreover, this is the only case of non-alkyl capped particles in which a microsecond lifetime was observed, albeit together with a nanosecond component.

A very recent development of the chemistry of SiNPs surface has been the incorporation of conjugated molecules through Si-C bond formation involving sp<sub>2</sub> carbons, starting from H-terminated SiNPs and organolithium reagents<sup>29</sup>. No difference was observed both in the photophysics and in the band gap energy measured trough single crystal scanning tunneling spectroscopy (STS) between alkyl and aryl derivatized samples, implying no influence of the aromatic group on the band gap. In the case of phenylacetylene however, an in-gap state was observed (*Figure 1.19(b)*), leading to a redshift of the luminescence. The quantum yield was found to decrease, while the luminescence lifetime was increased, with respect to the alkyl analogue. The realization of such a system is particularly important since it opens a way to a direct integration between silicon nanoparticles and organic conjugated materials, with promising application in the field of optoelectronics.

After this short discussion on the properties of silicon nanoparticles and on the strategies to tune their luminescence, we will move to the illustration of the integration of nanomaterials in artificial photosynthetic schemes, the broad field in which our approach for integrating molecules and nanomaterials can be inserted, focusing when possible on silicon and platinum nanoparticles, the two systems that will be used in our experimental work.

#### **1.4** General features of photosynthesis

In this thesis work, we will focus on the interaction between chromophores and nanoparticles for light energy conversion. This field is huge and implies different types of transformations, such as light to electrons, light to thermal energy or light to motion<sup>30,31</sup>.

Another major distinction can be made between heterogeneous systems, implying the use of photoactive surfaces in applications such as photovoltaics or photocatalysis, or homogeneous systems, in which the same functions are performed by molecular, supramolecular or nanoscale components (in this last case sometimes defined as "microheterogeneous" systems) dissolved in an appropriate solvent.

<sup>&</sup>lt;sup>28</sup>Wang, L. et al. (2015). Light: Science & Applications 4, e245.

 $<sup>^{29}\</sup>mathrm{Ang1}, \mathrm{A.}$  et al. (2016). Nanoscale.

 $<sup>^{30}</sup>$ Balzani, V. et al. (2008). ChemSusChem 1, 26–58.

<sup>&</sup>lt;sup>31</sup>Armaroli, N. et al. (2016). Chemistry–A European Journal 22, 32–57.



Figure 1.19: (a) Effect of different surface ligands on the photophysical properties of 3 nm SiNPs. (b) STS scans for phenyl (above) and phenylacetilene (below) terminated nanoparticles. An in-gap level is clearly visible in the latter, near the conduction band. (Images reprinted and adapted with permission form ref (29)).

In this work we decided to follow a specific path to light energy conversion, that of artificial photosynthetic systems in solution, because of two main reasons:

- The importance of the mimicking of the functions of natural photosynthesis for the transition to a sustainable society, due to the tremendous possibilities that the huge amount of light hitting the Earth surface would open if cleverly used to produce fuels and valuable chemicals<sup>31</sup>.
- The didactical value of the discussion on the various functions and processes required to realize a complete photosynthetic event. In fact, the precise integration of light harvesting, charge separation and catalysis allows a discussion that spans all the important parameters and phenomena that should be taken in consideration in most types of solar devices (e.g. photoinduced electron transfer processes are of utmost importance for solar cells or photocatalysis of organic chemistry transformations, while energy transfer is widely exploited in the field of sensors).

In natural systems  $^{32-36}$ , the photosythetic process can be divided in two parts:

- The light induced charge separation and generation of oxygen and the electronic mediator NADPH (alternatively, some enzymatic systems can catalyse the production of hydrogen instead of the reduction of NADP<sup>+</sup> to NADPH).
- The "dark" reaction cycles that make use of NADPH to generate valuable chemicals (e.g. glucose from CO<sub>2</sub> fixation).

The overall reaction in natural photosynthesis involves the reduction of  $CO_2$  to carbohydrates, that can be considered the "fuel" of many form of life on Earth, and follows the general equation:

$$CO_2 + 2H_2X + h\nu \longrightarrow (CH_2O) + 2X + H_2O$$
 (1.3)

where  $H_2X$  represents a general reductant ( $H_2O$ ,  $H_2S$ , MeOH ...).



Figure 1.20: A schematic side view of the transmembrane photosynthetic apparatus in plants (Reprinted with permission form ref (36)).

In plants light is absorbed by a so called "antenna-system", a series of membrane proteins containing circular arrangements of chromophores (chlorophylls and carotenoids), that are able to funnel the excitation energy towards a "special pair" consisting of a

 $<sup>^{32}\</sup>mathrm{McConnell},$  I. et al. (2010). Chemistry & biology 17, 434–447.

<sup>&</sup>lt;sup>33</sup>Zinth, W. et al. (2005). ChemPhysChem 6, 871–880.

<sup>&</sup>lt;sup>34</sup>Ritz, T. et al. (2002). ChemPhysChem 3, 243–248.

<sup>&</sup>lt;sup>35</sup>Barber, J. (2009). Chemical Society Reviews 38, 185–196.

<sup>&</sup>lt;sup>36</sup>Allen, J. F. et al. (2011). Trends in plant science 16, 645–655.
dimer of chlorophylls. This is the first component of the reaction center of photosystem II (PSII), a transmembrane protein in which a series of electron transfer steps generate a charge separation. The electrons are collected by a "quinone pool" (i.e. quinones present in the membrane), while the "holes" are accumulated on the so called "oxygen evolving complex" (OEC), a molecular cluster of manganese and calcium with the unique ability to oxidize water to oxygen. The electrons collected by the quinones are then transferred to a second transmembrane protein, the photosystem I (PSI), where a second light-induced electron transfer cascade leads to the reduction of NADP<sup>+</sup> to NADPH (or alternatively to the production of hydrogen through hydrogenases in some bacteria).



Figure 1.21: A general scheme of the functions that have to be performed by a photosynthetic system (Reprinted with permission form ref (31)).

While the description of the structural and energetic features of natural photosynthetic systems is well beyond our purposes, its observation allows to make some considerations related to its main functions:

- *Light harvesting.* The absorption of light over a large spectral interval and the efficient delivery of excitation energy to the reaction center.
- *Charge separation*. The series of cascade electron transfer processes occurring in the photosystems, to produce a spatially separated and long lived charge separation to be exploited in redox processes.
- *Catalysis.* The charges delivered to the catalysts are exploited to reduce NADP<sup>+</sup> to NADPH (or H<sub>2</sub>O to H<sub>2</sub>) after accumulation of two electrons and to oxidise H<sub>2</sub>O to O<sub>2</sub> after accumulation of four "holes".

The integration of the three separated processes in a single and efficient photosynthetic apparatus implies an high degree of organization:

- Spatial organization. The circular arrangement of the pigments in the antenna complexes, the precise spatial positioning of the cofactors participating to the charge separation processes in the transmembrane complexes and the compartmentalization provided by the membrane, with the reductive and oxidative catalytic processes happening on opposite sides, are essential for ensuring the efficiency of the photoinduced processes and prevent side reactions.
- Energetic organization. Probably the real essence of photosynthesis is to "reverse" a reaction that would otherwise be strongly thermodinamically favoured (e.g. the reaction of hydrogen and oxygen to form water, whose equilibrium constant is strongly shifted towards the product) and generate highly energetic species. This would be impossible without the addition of external energy in the form of photons. However, not all the energy absorbed is stored in the final products, but each step is associated with losses, passing from highly energetic excited states in chromophores to progressively less energetic charge separated states and chemical bonds.
- Temporal organization. In photosynthesis the time scale is overall very wide, passing from the very fast photoinduced energy transfer processes in antennas (fs to ps) to the charge-separation steps (ps to ns), to the redox processes in the quinone pool ( $\mu$ s). This illustrates very well the progressive energetic stability of the species involved and the necessity of coupling very short-lived excited states to charge-separated systems that can promote the relatively slow reactions happening on the catalytic moieties.

While the photosynthetic apparatus is an extremely elegant system that combines specialized functions with a high degree of precision and can be considered the natural "machine" that has allowed the development of oxygenic life on Earth and provided nearly all the energy sources that fueled the industrial society, it can be considered as a very delicate precision clock, more than a robust engine.

In fact, despite 2.5 billions of years of evolution, PSII still has to deal with highly energetic intermediates and extremely oxidizing species, arriving to the point of concentrating four "holes" on a single metal cluster. This extreme environment strongly damages the protein, that needs to be substituted about every 20 minutes<sup>32</sup>.

While nature has several strategies to minimize and repair photodamage<sup>37</sup> and the clear "success" of oxygenic life on Earth proves that photodamage is a "solved problem"

<sup>&</sup>lt;sup>37</sup>Takahashi, S. et al. (2011). Trends in plant science 16, 53–60.

in natural systems, this aspect is of utmost importance in the development of efficient and durable artificial analogues.

Following this general principles, scientists have tried to develop an artificial photosynthetic system for the conversion of solar energy into valuable fuels. The general requirements for a really sustainable process are the abundance, low cost, wide geographical distribution and low toxicity of the starting material, together with the quality of the resulting product as fuel (in terms of cost, ease of transportation and storage, pollution deriving from its use etc.).

The two processes that are widely regarded as the most promising are  $CO_2$  reduction, that would lead to the production of carbon-containing fuels and basic building blocks for organic chemistry transformation (eq. 1.4 to 1.7), and water splitting into hydrogen and oxygen (eq. 1.8):

$$CO_2 + 2H^+ + 2e^- \longrightarrow HCOOH$$
 (1.4)

$$CO_2 + 2H^+ + 2e^- \longrightarrow CO + H_2O$$
 (1.5)

$$CO_2 + 6H^+ + 6e^- \longrightarrow CH_3OH + H_2O$$
 (1.6)

$$2CO_2 + 4H_2O \longrightarrow 2CH_3OH + 3O_2 \tag{1.7}$$

$$2H_2O \longrightarrow 2H_2 + O_2 \tag{1.8}$$

In particular hydrogen production through water splitting would be a very valuable tool for the development of an "hydrogen economy", probably the most promising alternative to fossil energy in the field of fuels<sup>38</sup>.

In the following sections we will discuss some of the efforts made by scientists to reproduce photosynthesis, focusing on water splitting and dividing the sections based on the three functions described above. We will consider three main approaches: the molecular, the biomolecular and the nanotechnological one, with a particular emphasis on those cases in which their mutual integration was attempted.

In every section we will try to stress the fundamental problems related to the specific function and in particular how inorganic nanoparticles can be beneficial for the efficiency of the process, but what really constitutes a great advantage of inorganic nanosystems is their robustness with respect to photochemical and chemical degradation, an issue that appears to be a very serious drawback for molecules and biomolecules containing organic moieties.

<sup>&</sup>lt;sup>38</sup>Armaroli, N. et al. (2011). ChemSusChem 4, 21–36.

## 1.5 Light harvesting and charge separation

In the first phases of photosynthesis, solar light is harvested by antenna systems and transferred to a charge-separating unit. These two phenomena are obtained through a series of steps of energy and electron transfers between appropriately designed units. Since the two processes may be in competition and lead to inefficient systems if the energetic and spatial requirements for the involved states are not correctly fulfilled, it is very difficult to separate them in the following discussion and often we will describe systems in which the two functions are integrated.

#### 1.5.1 Light harvesting

Focusing on light harvesting, the main requisites for an efficient antenna system are:

- A wide absorption spectral interval. The highest is the absorption coefficient of the antenna system in the interval of wavelengths hitting the Earth surface, the most of the incident light will be effective in photosynthesis.
- Efficient and directional energy transfer processes between the antenna components.
- An accurate frequency match between photon absorption and the charge separation processes. In fact, in conditions of low irradiation, the frequency of excitation of the reaction center might be too low to have an efficient system, while in the case of too high irradiation the accumulation of excited states in the system might produce photodamage.

An example of molecular systems particularly efficient in promoting directional energy transfer and light absorption over a large spectral interval is constituted by dendrimers and dendrons (a branch of a dendrimer)<sup>39</sup>. This type of architecture is constituted by a central core, from which a certain number of branches departs. Each branch can then split in two or more "second generation" branches, and so on, generating a tree-like structure.

Due to the high degree of control achievable by the synthetic protocols developed for dendrimeric structures, a large number of chromophores can be included in a single dendrimer and each branching point can contain a different type of molecule, thus producing a very precise and structurally ordered system.

In the dendrimer shown in Figure 1.22(a), the different chromophoric units are linked together through saturated chains and thus behave as isolated molecules (i.e.

<sup>&</sup>lt;sup>39</sup>Balzani, V. et al. (2003). Current opinion in chemical biology 7, 657–665.



Figure 1.22: (a) An example of host-guest dendrimer-based light harvesting antenna (Reprinted with permission form ref (39)). (b) A conjugated light harvesting dendron (Reprinted with permission form ref (40)).

there is no mixing of the orbitals of different chromophores). Upon absorption of light by the peripheral naphtalene and dimethoxybenzene units, energy is transferred to the dansyl moieties with a 90% efficiency. Interestingly, the poliamminic core is able to incapsulate a molecule of Eosin, that becomes the final energy acceptor (80% efficiency from the dansyls), thus realizing a directional and efficient antenna effect<sup>41</sup>.

A different approach is shown in Figure  $1.22(b)^{40}$ . Even in this case an energetic gradient provides the driving force for an efficient localization of the electronic energy in the central perylene, but the different units composing the dendron are linked together through conjugated acetylene links and the system can be though as a big molecule, in which there is a significant interaction between the electronic clouds of the individual parts in the ground state. Upon light absorption, the excited state is delocalized all over the molecule, and subsequently localizes, in a two step process driven by conformational changes, on the perylene. This dendron constitutes also a model for the study of exciton dynamics in cojugated polymers and other materials with large  $\pi$  systems.

#### 1.5.2 Charge separation

Switching our attention on charge separation, the most important requirements for an efficient mimic of the natural reaction center are:

• A spatial organization that ensures a progressive separation between the positive

<sup>&</sup>lt;sup>41</sup>Hahn, U. et al. (2002). Angewandte Chemie International Edition 41, 3595–3598.

<sup>&</sup>lt;sup>40</sup>Galindo, J. F. et al. (2015). Journal of the American Chemical Society 137, 11637–11644.

and negative charges.

- A proper match of the energies of the charge separated states to maximize separation processes and minimize the detrimental charge recombinations. The key point to achieve this goal is to have a sufficient thermodynamic driving force to ensure a fast charge separation without losing too much of the initial absorbed energy, while at the same time keeping the driving force for charge recombination high enough to fall in the so-called "Marcus inverted region", in which the processes are kinetically slow (and thus less competitive).
- The possibility to realize charge accumulation phenomena, to couple the oneelectron photoinduced processes with the multielectronic catalytic reactions. In many systems, this function is performed by the catalyst itself, but some cases have been reported in which a dedicated molecular unit is introduced.



Figure 1.23: A charge separation triad (above) and the energy scheme of the states involved (below) together with arrows indicating the possible competing processes (Reprinted with permission form ref (30)).

A good example of molecular charge separation systems is represented by the triad shown in *Figure 1.23*<sup>42</sup>. The absorption of light by the central porphyrin leads to an electron transfer process to reduce the fullerene unit. Following this step, a second electron transfer occurs from the carotenoid to the oxidized porphyrin, leading to the final charge-separated state  $C^+$ -P- $C_{60}^-$  with an overall quantum efficiency of 88%. This is possible thanks to the favourable competition between the final charge separation

<sup>&</sup>lt;sup>42</sup>Liddell, P. A. et al. (1997). Journal of the American Chemical Society 119, 1400–1405.

step (8 in *Figure 1.23*) and the charge recombination between the oxidized porphyrin and the reduced fullerene (7 in *Figure 1.23*) which is slower because its thermodynamic driving force falls into the Marcus inverted region. The final charge separated state has a lifetime of about 345 ns, before decaying to the carotenoid triplet.

#### 1.5.3 Molecular systems



Figure 1.24: (a) A porphyrin array coupling light harvesting and charge separation (Reprinted with permission form ref (30)). (b) A dendrimeric system integrating light harvesting, charge separation and charge accumulation (Reprinted with permission form ref (43)).

Light harvesting and charge separation have been integrated in complex systems. In the porphyrinic array shown in *Figure 1.24(a)*, absorption of light by the peripheral porphyrins (pZnP) lead to energy transfer processes to the central Zn porphyrin (cZnP) and then to the free base porphyrin (H<sub>2</sub>P). Following this energy harvesting, a first electron transfer occurs from H<sub>2</sub>P to fullerene, followed by a second from cZnP to H<sub>2</sub>P, thus resulting in a final charge-separated state  $cZnP^+-H_2P-C_{60}^-$  with 86% quantum efficiency. The state decays to the ground state with a lifetime of 240 ns.

The dendrimer shown in Figure 1.24(b) performs a similar task, with the peripheral zinc porphyrins transfering energy to the central free base porphyrin (86% efficiency), from which a sequential electron transfer series leads to the localization of an electron on the central polioxometalate (POM) complex and of the hole on a peripheral porphyrin. What is most interesting in this system is that upon reaction with a sacrificial electron donor (triethanolamine, TEOA) the neutrality of the porphyrin is restored and a second photoinduced process can occur, leading to the accumulation of two negative charges

on the POM unit<sup>44</sup>.

#### 1.5.4 Nanoparticle-based systems

In the field of nanomaterials, a particularly attractive alternative to molecular antennas is represented by direct band gap semiconductor quantum dots. This type of materials in fact have a much larger absorption cross section and a greater photostability with respect to organic dyes and their band gap can be easily modulated through size  $control^{45}$ .

For this reason, they are regarded as particularly attractive for the field of luminescent sensors<sup>45-47</sup> and several examples are reported in which they interact with molecular species either by energy or electron transfer. Being that the same processes are involved in photosynthesis, these example can be considered as a direct proof of the applicability of QDs as components for light harvesting and charge separation systems.



Figure 1.25: (a) A QD-molecule system showing acid/base switchable energy transfer (Reprinted with permission form ref (47)). (b) A QD acting as light harvesting unit to enhance the photoactivity of a bacterial RC complex (Reprinted with permission form ref (48)).

For example, the system shown in *Figure 1.25(a)* bases its pH sensing ability on the protonation/deprotonation controlled switching of an energy transfer process from a

<sup>&</sup>lt;sup>44</sup>Elliott, K. J. et al. (2009). Physical Chemistry Chemical Physics 11, 8767–8773.

<sup>&</sup>lt;sup>45</sup>Medintz, I. L. et al. (2005). Nature materials 4, 435–446.

<sup>&</sup>lt;sup>46</sup>Zhou, J. et al. (2015). Chemical reviews 115, 11669–11717.

<sup>&</sup>lt;sup>47</sup>Silvi, S. et al. (2015). *Chemical Society Reviews* 44, 4275–4289.

CdSe/ZnS core-shell QD to a squaraine acceptor molecule. An elegant example showing the use of QDs as antenna is reported in *Figure 1.25(b)*, in which a CdSe or CdTe quantum dots has been coupled to a bacterial RC complex, leading to an enhancement of the complex photoactivity due to an energy transfer process from the nanocrystal to the special pair of the protein<sup>48</sup>.

A different approach to the construction of nanoparticle based organic-inorganic light harvesting antennas has been explored by our group in the case of silicon nanoparticles. Contrarly to direct band gap QDs, silicon nanoparticles present a relatively weak absorption in the visible range, making them unsuitable for acting as absorbers. Interestingly however, their excited state lifetime is much longer than that of direct band gap QDs  $(10^{-5}-10^{-4} \text{ s vs } 10^{-8}-10^{-7} \text{ s})$ , allowing the coupling of the fast energy harvesting processes to relatively slow diffusion-controlled processes in solution.

In this case the use of visible light organic absorbers results in an increase in the absorption ability of the nanoparticle due to energy transfer processes, as observed for example in the case of pyrene appended  $SiNPs^{49}$ , in which red emissive 2.6 nm SiNPs and NIR emissive 5 nm SiNPs have been proven to be able to act as energy transfer acceptors upon pyrene excitation with efficiencies of 95% and 65% respectively. What is remarkable is that a relatively large number of chromophores can be attached to the same nanoparticle (about 7 for 2.6 nm and about 60 for 5 nm SiNPs), leading to the possibility of realizing hybrid systems with a very high brightness in the red-NIR region due to the combined effect of the enhanced absorption cross section and high PL quantum yield of the SiNPs (about 10% for 2.6 nm and about 45% for 5 nm SiNPs).

Moreover, this approach has been extended by the exploitation of the ability of pyrene units to form  $\pi - \pi$  stacking interactions with carbon nanomaterials<sup>50</sup>. In particular, pyrene functionalized SiNP's emission is statically quenched by both carbon nanotubes and graphene, indicating the occurrence of the association, even though it was not possible to distinguish if the quenching process is due to energy or electron transfer. A different behaviour was observed for fullerene. In this case in fact, the quenching occurred dynamically (i.e. following a collision event in solution), and the formation of singlet oxygen was used to confirm that the main mechanism is an energy transfer process to the fullerene triplet excited state (*Figure 1.26*). This finding proves the possibility of SiNPs to act both as acceptors and donors in light harvesting systems, even involving triplet states.

A peculiar approach for the integration of nanomaterials in light harvesting systems is based on the use of plasmonic nanoparticles, which are able to locally enhance the

<sup>&</sup>lt;sup>48</sup>Nabiev, I. et al. (2010). Angewandte Chemie International Edition 49, 7217–7221.

<sup>&</sup>lt;sup>49</sup>Locritani, M. et al. (2014). The journal of physical chemistry letters 5, 3325–3329.

<sup>&</sup>lt;sup>50</sup>Mazzaro, R. et al. (2015). Chemistry of Materials 27, 4390–4397.



Figure 1.26: A pyrene-SiNP antenna capable to transfer excitation energy to a fullerene acceptor upon diffusion-controlled encounter in solution (Reprinted with permission form ref (50)).

effect of the optical field, leading to an increase of the absorption coefficients of nearby chromophores and consequently of the efficiency of photosynthetic systems, like in the example shown in *Figure 1.27(a)*, in which gold and silver nanoparticles have been used to enhance the absorption cross section of PSI over a wide wavelength range<sup>51</sup>. A very elegant example of a nanostructured antenna (*Figure 1.27(b)*) was reported, in which DNA strands were used to modulate the distance between a central gold nanoparticles and peripheral CdSe/ZnS core-shell QDs<sup>52</sup>. This system produces a different response when subjected to different light stimuli. Upon irradiation at the plasmon resonant frequency in fact, an enhancement of the QD brightness due to an increase of both absorption and emission was observed, while upon excitation at an off-resonance wavelength a quenching due to energy transfer from the QDs to the gold nanoparticle lead to a decrease of the emission intensity. Both processes were found to be controllable by variation of the DNA spacer length.

## 1.6 Catalysis

#### **1.6.1** General principles

Besides the necessity to achieve a long-lived charge separation, its exploitation needs appropriate catalysts to induce chemical reactions that will result in the definitive

<sup>&</sup>lt;sup>51</sup>Carmeli, I. et al. (2010). Nano letters 10, 2069–2074.

 $<sup>^{52}</sup>$ Sun, D. et al. (2015). ACS nano 9, 5657–5665.



Figure 1.27: (a) A picture showing the interaction of a gold nanoparticle (in the center) with three PSI complexes. (Reprinted with permission form ref (51)). (b) A gold NP-QD antenna assembled using DNA strands (Reprinted with permission form ref (52)).

storage of the absorbed energy in form of chemical bond. For water splitting purposes, this means the necessity of an oxygen evolving catalyst (OEC) and of an hydrogen evolving one (HEC). From the observation of the corresponding natural systems, i.e. the Ca-Mn oxygen evolving cluster in PSII and the Fe-Fe or Fe-Ni dimer of hydrogenases, a few requirements emerge for efficient catalysis<sup>53</sup>:

- The necessity to couple monoelectronic light induced charge separation processes with multielectronic catalytic reactions. In particular H<sub>2</sub> evolution requires 2e<sup>-</sup> while O<sub>2</sub> production requires 4 "holes". To realize the required charge accumulation, it is important that each monoelectronic process happens about with the same potential. Since one would expect the potential to become progressively more unfavourable upon addition of charges of the same type on a single molecular species, some "charge-balancing" mechanism has to be involved. In particular proton coupled electron transfer (PCET), the concomitant transfer of a nearby hydrogen atom upon electron transfer, plays an important role.
- The importance of the cavity surrounding the catalysts for the diffusion of the reagents and products, for their activation through specific binding and for the protection from degradation.

<sup>&</sup>lt;sup>53</sup>Lubitz, W. et al. (2008). Energy & Environmental Science 1, 15–31.

• The advantage presented by metallic clusters. In fact the vicinity of metals can be beneficial to the appropriate positioning of reacting adsorbed reagents and intermediates to drive the product formation.

In the study of solar water splitting reactions, one should sensitize the catalyst through photoinduced electron transfer, so every system that will be presented is essentially an half-cycle of the full photosynthetic system. To evaluate the quality of a catalyst as OEC or HEC it is in fact important to avoid that a poor performance of the system is due to a bad integration (in terms of reaction rate matching and parasite processes) of the reductive and oxidative pathways. This is achieved through the use of sacrifical electron donors (SED) or acceptors (SEA) that mimic the "missing" part of the overall process, following the scheme shown in *Figure 1.28*.



Figure 1.28: The general scheme of photocatalysis experiments (Reprinted with permission form ref (54)). The acronym "WOC" (water oxydation catalyst) is what is called OEC in the text, while CRC stands for "carbon reducing catalysts".

For catalytic systems, a few parameters are mostly used to judge their efficacy and suitability for real applications 55,56:

- *Turnover Number (TON)*. It's the number of catalytic cycles performed by the catalyst before its inactivation.
- Turnover Frequency (TOF). In "dark" chemical reactions it's the number of catalytic events per unit time. In photocatalyzed reactions this concept is slightly more complicated because the rate of excitation of the system (directly dependent on the photon flux) has to be considered as the highest limit, since a catalytic event can be produced only if a photon is absorbed. It is possible to take into consideration this aspect in two ways. Dividing the TOF for the number of *incident* photons hitting the sample per second, one obtains the "quantum efficiency" (or

<sup>&</sup>lt;sup>55</sup>Swierk, J. R. et al. (2013). Chemical Society Reviews 42, 2357–2387.

<sup>&</sup>lt;sup>56</sup>McDaniel, N. D. et al. (2010). *Dalton Transactions 39*, 10021–10030.

"external quantum efficiency", EQE) of the system. To take into consideration only the "useful" photons, and thus evaluate the performance of the system upon excitation, one can divide the TOF by the number of *absorbed* photons per second, obtaining the so-called "quantum yield" (or "internal quantum efficiency", IQE) of the system.

- *Reaction overpotentials.* It's the excess energy per unit charge that must be added to drive the process as the catalyst cycles. In practice this is often measured as the difference between the onset of the catalyzed reaction (in terms of potential in an electrocatalysis experiment) and the formal potential for the reaction at the pH where the system is operated.
- *Power efficiency*. It's the ratio between the absorbed energy and the amount of energy stored in the final products and depends on the redox potentials of the involved species (including the sacrificial reagents) and on the quantum efficiency of the system.

In practice, the TON number and the cost per gram of the catalyst should be taken together to assess the suitability of the system for cheap hydrogen production<sup>56</sup>, but TONs in the order of  $10^9$  should be reached for a device that can operate for 20-30 years<sup>55</sup>. The optimal TOF at sunlight intensities depends on the absorption of the system and on the number of electrons exchanged in the overall cycle, but a value of at least  $10^2$ - $10^3$  events per second should be reached<sup>55</sup>. The TOF value should be considered as one of the most critical parameters, since the fastest the catalytic process is, the best it can compete with unwanted processes such as degradation.

It is however important to stress again the fact that it is often difficult to compare different catalysts based on TON or TOF, due to the fact that both parameters can be limited by factors that are not dependent upon the catalyst itself, such as the rate of the processes that reduce or oxidize it (a typical example is the case of diffusion limited systems) or the degradation of the photosensitizer, so these parameters should be used more correctly to describe the performance of the overall system.

#### 1.6.2 Molecular catalysts

The field of molecular catalysts for water splitting (either photocatalytic or electrocatalytic) is huge and very active<sup>54,55,57</sup>. A full discussion of the different types of catalysts and of their relative performance is out of the scope of this work. Moreover

<sup>&</sup>lt;sup>54</sup>Berardi, S. et al. (2014). Chemical Society Reviews 43, 7501–7519.

<sup>&</sup>lt;sup>57</sup>Eckenhoff, W. T. et al. (2012). *Dalton Transactions* 41, 13004–13021.

a comparison between different systems is not easy due to the fact that catalysts are studied in different environments (organic solvent with acids as proton sources, solvent/water mixtures or water at different pH values) and are sensitive to degradation in equally different conditions.

For these reasons, it is impossible to define "the best" catalysts. Here we will report a few representative examples that have been proven promising for their good performance in suitable conditions, then we will focus on the application of nanoparticles in solution and on their integration with molecular and biomolecular systems.

The first examples of a working photocatalytic hydrogen evolution system were reported in the late 70's<sup>58-60</sup>. The general scheme of their photoreductive cycle (*Figure 1.29*) involves the absorption of visible light by a metal complex photosensitizer featuring a long-lived triplet excited state, followed by its reduction by a sacrificial reductant. The reduced metal complex is then able to transfer electrons to a colloidal platinum catalyst through the assistance of an electron relay, a species capable to be reversibly reduced and oxidized at suitable potentials to allow the transport of electrons from the photosensitizer to the catalyst.



Figure 1.29: The general scheme of the early examples of water photoreduction (Reprinted with permission form ref (57)). The acronym "ED" stands for "electron donor", while "ER" stands for "electron relay".

However, despite the fact that Pt is a very good catalyst for hydrogen evolution, its high cost has pushed researchers to look for cheaper alternatives in the form of molecular catalysts based on Earth-abundant metals (Fe, Ni, Co, Mn, Mo...)<sup>54,57</sup>, or to reduce the size of platinum colloids to the nanoparticle regime, to enhance surface to volume ratio and thus reduce the amount of material required<sup>61,62</sup>.

A recent example is represented by the cobalt dithiolene complex shown in *Figure* 1.30(a), which is able to generate hydrogen with a TON > 2700 and an initial TOF of > 800 h<sup>-1</sup> in a 1:1 ACN/H<sub>2</sub>O mixture at pH = 4, using [Ru(bpy)<sub>3</sub>]<sup>2+</sup> as photosensitizer

<sup>&</sup>lt;sup>58</sup>Lehn, J. M. et al. (1977). Nouveau Journal De Chimie-New Journal of Chemistry 1, 449–451.

<sup>&</sup>lt;sup>59</sup>Moradpour, A. et al. (1978). Nouveau Journal De Chimie-New Journal of Chemistry 2, 547–549.

<sup>&</sup>lt;sup>60</sup>Kalyanasundaram, K. et al. (1978). *Helvetica Chimica Acta 61*, 2720–2730.

<sup>&</sup>lt;sup>61</sup>Crooks, R. M. et al. (2001). Accounts of Chemical Research 34, 181–190.

<sup>&</sup>lt;sup>62</sup>Astruc, D. et al. (2005). Angewandte Chemie International Edition 44, 7852–7872.

and ascorbic acid as sacrificial electron donor. In the same work, the cobalt complex was tested also as electrocatalyst in a CV experiment in the same solvent mixture, using trifluoroacetic acid (TFA) as a proton source. The system shows a faradic efficiency (the number of moles of product per mole of electrons injected in the system) of >99% at -1.0 V vs SCE of applied potential<sup>63</sup>.



Figure 1.30: (a) The cobalt dithiolene complex used in ref (63) (Reprinted with permission form ref (54)). (b) A water oxydation system based on a tetraruthenium POM catalyst showing exceptional activity (Reprinted with permission form ref (64)).

The field of water oxidation catalysis has been dominated for long time by the use of precious metals such as Ru or Ir, but more recently several successful examples have been reported using abundant elements<sup>54,65</sup>. Due to the difficulty of realizing a tetraelectronic oxidation, which implies the necessity of charge-balancing processes (such as PCET) and results in the facile degradation of organic ligands, water oxidation has been often defined as the "bottleneck" of the whole process, but promising results have been obtained using all-inorganic metal oxides, either in heterogenous <sup>66,67</sup> or homogeneous catalysis (interestingly, in several cases it has been reported that molecular metal complexes added as catalysts were actually precursors for the formation of metal oxide nanoparticles that acted as the real catalysts<sup>65</sup>). The polyoxometalate tetraruthenium complex shown in *Figure 1.30(b)* is able to drive water oxidation when combined to a ruthenium polymetallic dendrimer as sensitizer in a pH 7.2 aqueous buffer, using sodium persulfate as sacrificial electron acceptor<sup>64</sup>. Upon single-wavelength irradiation at 550 nm, an exceptional quantum yield of oxygen production of 60% was obtained. In this

<sup>&</sup>lt;sup>63</sup>McNamara, W. R. et al. (2011). Journal of the American Chemical Society 133, 15368–15371.

<sup>&</sup>lt;sup>65</sup>Wu, X. et al. (2015). Journal of Photochemistry and Photobiology C: Photochemistry Reviews 25, 71–89.

<sup>&</sup>lt;sup>66</sup>Osterloh, F. E. (2013). Chemical Society Reviews 42, 2294–2320.

<sup>&</sup>lt;sup>67</sup>Reece, S. Y. et al. (2011). *Science 334*, 645–648.

<sup>&</sup>lt;sup>64</sup>Puntoriero, F. et al. (2010). Chemical Communications 46, 4725–4727.

system, the very fast electron transfer reaction between the oxydized photosensitizer and the catalyst is responsible for the very high quantum yield and has been hypothesized to have a role in protecting the sensitizer from decomposition.



### 1.6.3 Nanoparticle-based systems

Figure 1.31: (a) The effect of size reduction on the charge recombination processes in photoexcited semiconductor nanoparticles (Reprinted with permission form ref (68)). (b) The effect of quantum confinement on the band gap in semiconductor nanoparticles (Reprinted with permission form ref (66)).

Semiconductor nanoparticles have been used in catalytic water splitting due to their peculiar properties  $^{66,68-72}$ :

- *Small size.* The reduced dimensions of the systems are fundamental to achieve a large surface/volume ratio, clearly a fundamental requirement for efficient surface-catalyzed processes. Moreover, since the generated exciton is always in proximity of the surface, charge recombination is decreased and charge injection through the surface is promoted, resulting in high current densities and low overpotentials.
- *High stability.* This is not true for all materials, and depends strongly on operating conditions, (e.g. pH is clearly a fundamental parameter to consider when using metal oxide nanoparticles in aqueous solution). Degradation may result in the destruction of the material or in the formation of surface localized trap states that can be detrimental for the catalytic efficiency. However in appropriate conditions the all-inorganic nature of nanoparticles makes them much more robust with

<sup>&</sup>lt;sup>68</sup>Maeda, K. (2011). Journal of Photochemistry and Photobiology C: Photochemistry Reviews 12, 237–268.

<sup>&</sup>lt;sup>69</sup>Grewe, T. et al. (2016). Chemistry-An Asian Journal 11, 22–42.

<sup>&</sup>lt;sup>70</sup>Bren, K. L. (2015). *Interface focus* 5, 20140091.

<sup>&</sup>lt;sup>71</sup>Zhang, X. et al. (2016). Journal of Materials Chemistry A.

<sup>&</sup>lt;sup>72</sup>Wang, M. et al. (2015). Coordination Chemistry Reviews 287, 1–14.

respect to organic or organometallic species towards photo or redox induced degradation.

- Size tunable properties. Electronic properties of nanomaterials are strongly dependent on their size and shape. In particular dimensional control is used to tune the energy of the valence and conduction bands of semiconductors in the quantum confinement regime, to achieve a better match with the redox potentials of the involved processes.
- Surface functionalization. The possibility to derivatize the surface of nanoparticles opens the possibility of realizing integrated systems comprising molecular catalysts and sensitizers. Moreover, the electrostatic effect of charged ligands may be used to further tune the electronic properties of the nanoparticle.



Figure 1.32: (a) The CdTe-QD/hydrogenase/chitosan system showing high TON for hydrogen evolution (Reprinted with permission form ref (73)). (b) The CdSe-QD/Ni(DHLA)<sub>2</sub> system showing exceptional TON for hydrogen evolution (Reprinted with permission form ref (74)).

A particularly successful example of integration of a semiconductor nanoparticle with a molecular hydrogen evolving complex is shown in *Figure 1.32(a)*. In this work a [Fe-Fe]-hydrogenase mimic was combined with carboxylate appended CdTe quantum dots at pH 4.5 in a 3:1 v/v MeOH/H<sub>2</sub>O mixture, using ascorbic acid as a sacrificial electron donor. A modest TON of 12.3 was obtained. Very interestingly, the addition of chitosan increased the the TON to 52800, combined with an initial TOF of 1.4 s<sup>-1</sup>. This was attributed by the authors to the effect of the charged cavity of chitosan in keeping the species in close proximity and facilitating electron transfer processes<sup>73</sup>.

<sup>&</sup>lt;sup>73</sup>Jian, J.-X. et al. (2013). Nature communications 4.

One of the most remarkable examples of integration between a semiconductor nanoparticle and a molecular catalyst was reported for a system composed of dihydrolipoic acid (DHLA) stabilized CdSe-QDs in presence of Ni(NO<sub>3</sub>)<sub>2</sub> in pH 4.5 water, using ascorbic acid as sacrificial donor (*Figure 1.32(b)*). The real catalytic species is most probably in this case a Ni(DHLA)<sub>2</sub> complex formed in-situ. This system shows an unprecedented TON of 600000, with an initial TOF of over 7000 h<sup>-1</sup>. The quantum yield for hydrogen production was 33% in water and 66% in a 1:1 EtOH/H<sub>2</sub>O mixture<sup>74</sup>.



Figure 1.33: (a) An Ir<sub>2</sub>O nanoparticle used as OEC, with a molecular specie mediating the electron transfer from the nanoparticle to the photosensitizer. (Reprinted with permission form ref (75)). (b) An hydrogen evolving system in which both the sensitizer and the cataòysts were molecular species anchored to the same TiO<sub>2</sub> nanoparticle (Reprinted with permission form ref (76)).

A different use of molecular species coupled to catalytic semiconductor nanoparticles is shown in *Figure 1.33(a)*, in which an Ir<sub>2</sub>O nanoparticle was used as water oxidation catalyst in combination with a ruthenium complex as photosensitizer. Both the species were anchored to a TiO<sub>2</sub> electrode, and upon irradiation charge injection from the excited photosensitizer to the TiO<sub>2</sub> conduction band triggers the electron transfer cascade that leads to oxygen evolution. The addition of a benzimidazole-phenol (BiP) electron mediator, capable of performing a proton coupled electron transfer process, substantially improves the performance of the system, with the internal quantum efficiency passing from 0.8% to 2.3%<sup>75</sup>.

Both the photosensitizer and the catalyst can be attached to the same semiconductor nanoparticle, that acts as an electron mediator between the two, such as in the system shown in *Figure 1.33(b)*, in which a ruthenium complex and a cobaloxime catalyst have

<sup>&</sup>lt;sup>74</sup>Han, Z. et al. (2012). Science 338, 1321–1324.

<sup>&</sup>lt;sup>75</sup>Zhao, Y. et al. (2012). Proceedings of the National Academy of Sciences 109, 15612–15616.

been anchored on the surface of TiO<sub>2</sub> nanoparticles through phosphonate groups  $^{77,78}$ . The system is able to drive the production of hydrogen at pH 7, usine tetraethanoammine as a sacrificial electron donor, with a TON of 108 based on the cobalt catalyst and a TOF of about 20 h<sup>-1</sup>. The relatively low TON value can be ascribed to the instability of the molecular components. The activity of the system dropped considerably when the anchoring phosphonate ligand on the catalyst was in the form of ethyl ester derivative (thus preventing the anchoring), clearly showing the advantage of linking molecular species to the same nanoparticle scaffold.



Figure 1.34: (a) A porphyrin-anthracene antenna coupled to a Pt nanoparticle for hydrogen evolution (Reprinted with permission form ref (79)). (b) A scheme of a PtNP/PSI self-assembled system performing hydrogen evolution, together with a picture showing hydrogen bubbles produced in solution upon irradiation (Reprinted with permission form ref (76)).

Metal nanoparticles have been coupled to molecular sensitizers to realize hydrogen evolving systems, like in the case of the porphyrin-antracene derivative shown in *Figure* 1.34(a), that is able to assemble on the surface of Pt nanoparticles<sup>79</sup>. This system is a nice example of coupling of photosynthetic functions. In fact, energy transfer from the anthracene units to the central porphyrin occurs with nearly quantitative efficiency (mimicking the antenna system), followed by the charge separation and catalysis events. Hydrogen evolution was run in 1:1 EtOH/H<sub>2</sub>O mixture, using EtOH itself as sacrificial electron donor, thus avoiding the need for additives. Even though TON and TOF values were not reported, the system appeared to be highly stable in repeated ON/OFF catalytic cycles. Moreover, the necessity of an electron mediator between the sensitizer and the catalyst was completely eliminated.

Metal nanoparticles can be used as well to enhance the catalytic activity of natural

<sup>&</sup>lt;sup>77</sup>Lakadamyali, F. et al. (2012). Faraday discussions 155, 191–205.

<sup>&</sup>lt;sup>78</sup>Lakadamyali, F. et al. (2012). Chemistry-A European Journal 18, 15464–15475.

<sup>&</sup>lt;sup>79</sup>Zhu, M. et al. (2013). Catalysis Science & Technology 3, 2295–2302.

photosystems. A self-assembled Pt-NP/Photosystem I has been proven particularly promising in hydrogen production in pH 6.2 water buffered solution, using cytochrome 6 as a redox mediator and ascorbate as sacrificial electron donor (*Figure 1.34(b)*). The system showed a remarkable TOF of more than 20000 h<sup>-1</sup> based on PSI<sup>76</sup>.



Figure 1.35: (a) The "Z-scheme" approach in which an electron mediator shuttles between two nanoparticles with suitably aligned band gaps. (b) A solar cell scheme in which the electron mediator is replaced by a couple of mediators connected by a conductive wire. (Images reprinted with permission form ref (80)).

Several examples have been reported in which semiconductor nanoparticles with different band gaps have been coupled to realize the so-called "Z-scheme"<sup>80</sup>, that involves the absorption of two different photons, mimicking what happens in in nature in PSII and PSI. The general working scheme of such a system is reported in *Figure 1.35(a)*, and involves the presence of an electron mediator (the quinone pool in natural systems) to shuttle charges from one particle to the other. The rationale behind this approach is that a nanoparticle may have a band gap suitable for water reduction but not for its oxidation, while the reverse may happen with a second type of nanoparticle. Each of the nanoparticles, taken singularly, would never be able to realize a complete water splitting cycle, but the "connection" of the particles by the mediator results in a system in which both reduction and oxidation can occur, each on the appropriate type of nanoparticle.

This general approach has been extended by realizing a solar cell in which the reduction and oxidation semicells were connected by a conductor wire and separated by a proton exchange membrane<sup>81</sup>. This design is based on the same type of compartmentalization shown in natural system, with the reduction and oxidation reactions happening in physically separated places, avoiding unwanted reactions between the components of each cycle. In this first reported example, Pt-loaded TiO<sub>2</sub> nanoparticles were used in combination with the Br<sup>-</sup>/Br<sub>2</sub> redox couple in the hydrogen evolving

<sup>&</sup>lt;sup>76</sup>Grimme, R. A. et al. (2008). Journal of the American Chemical Society 130, 6308–6309.

<sup>&</sup>lt;sup>80</sup>Maeda, K. (2013). ACS Catalysis 3, 1486–1503.

<sup>&</sup>lt;sup>81</sup>Fujihara, K. et al. (1998). Journal of the Chemical Society, Faraday Transactions 94, 3705–3709.

cell, while TiO<sub>2</sub> nanoparticles and the Fe<sup>II</sup>/Fe<sup>III</sup> redox couple were used in the oxygen evolving cell. While the system is far from being optimal (e.g. TiO<sub>2</sub> doesn't absorb light in the visible range and contamination on the Pt connecting wire lowered the efficiency), water splitting has been demonstrated, opening promising perspectives.



Figure 1.36: The "hydrogen on demand" system based on SiNPs, showing the whole cycle from SiNP production to the final electric energy supply generated by a fuel cell. (Reprinted with permission form ref (82))

#### 1.6.4 The possible role of silicon nanoparticles

To the best of our knowledge, silicon nanoparticles have never been applied in homogeneous photosynthetic systems. As observed before, in principle the ability to act as energy transfer acceptors and their long lived excited state lifetime should be beneficial for applications in homogenous catalysis based on diffusional electron transfer processes. However, silicon nanoparticles with diameter below 10 nm have been reported to fastly decompose in water environment and since this reaction involves the evolution of hydrogen, they have been proposed as hydrogen generating materials for "on-demand" hydrogen supply from water, simply adding a KOH aqueous solution in a tank containing silicon nanoparticles<sup>82</sup>.

This problem could be overcome with an appropriate protective surface functionalization, or alternatively SiNPs could find application in other areas of catalysis

<sup>&</sup>lt;sup>82</sup>Erogbogbo, F. et al. (2013). Nano letters 13, 451–456.

usually performed in organic solvents, such as in the rapidly growing field of photoredox catalysis<sup>83</sup>. This type of chemistry is analogous to what we have described for water splitting systems, with the difference that the reduced or oxydized species that are formed upon photoredox processes undergo radicalic organic chemistry reactions instead of evolving hydrogen or oxygen (*Figure 1.37*).



Figure 1.37: (a) The general scheme of the possible pathways of a photoredox reaction, based on the quenching process involving the photosensitizer  $([Ru(bpy)_3]^{2+}$  in this case). (b) One of the earlier examples of a photoredox reaction, a dehalogenation reaction in presence of a sacrificial electron donor<sup>84</sup>. (Images reprinted with permission form ref (83)).

In this type of reactions phosphorescent precious metal complexes (commonly Ru or Ir) with long lifetimes are often used to have efficient diffusional electron transfers (fluorescent dyes are sometimes used due to their low cost, but their lifetimes in the nanosecond regime make the process rather inefficient from a point of view of photon to molecule conversion). The triplet states involved in the process are easily quenched by oxygen, potentially leading to the very reactive singlet oxygen.

Silicon nanoparticles have the advantage of presenting an excited state lifetime much longer than typical organometallic sensitizers and their emission properties are totally insensitive to the presence of oxygen. Moreover, their band gap, and thus redox potentials, may be tuned by size control, with different sizes that might be appropriate for different reactions.

The possibility of realizing efficient antenna systems involving a large number of chromophores leads to a potentially excellent system. In fact, highly emissive organic

<sup>&</sup>lt;sup>83</sup>Prier, C. K. et al. (2013). *Chemical reviews 113*, 5322–5363.

molecules, such as fluoresceine or rhodamines, normally have absorption coefficients in the order of  $10^{4}$ - $10^{5}$  cm<sup>-1</sup> M<sup>-1</sup> at the maximum of the lowest energy band. By attaching a large number of this chromophores to SiNPs and supposing high energy transfer efficiencies (by using a rather inefficient approach we were able to attach up to 60 pyrene molecules to a 5 nm SiNP with energy transfer efficiencies of 65%), the apparent absorption coefficient (i.e. the sum of the absorption coefficients of the attached chromophores multiplied by the energy transfer efficiency) of the SiNP could rise to the  $10^{6}$ - $10^{7}$  cm<sup>-1</sup> M<sup>-1</sup> range.

Since the efficiency of the electron transfer process involving the sensitizer doesn't depend on its concentration (but only on its excited state lifetime) and the rate of the reaction is proportional to the rate of excitation (that depends on the light source intensity and the photosensitizer's absorbance), a SiNP-based antenna system like the one described above would result in a very efficient use of the exciting light, leading to several possibilities:

- A reduction of the photosensitizer's concentration, leading to a decrease of the associated economic impact in view of a future industrial application. This also implies the possibility of lowering the reagents' concentration while always keeping the "large excess" condition with respect to the sensitizer, reducing the amount of compound needed for laboratory tests and overcoming possible solubility issues. Moreover recombination and degradation processes that depend on the sensitizer's concentration become less likely.
- A lowering of the intensity and a narrowing of the spectral distribution of the light source, thanks to the very intense and narrow absorption band of the antenna chromophores. This would lead to a reduction of the energetic cost of the process and of the photodamage that could affect the organic species in solution.
- An increase of the reaction speed. In the presence of high concentration of the photosensitizer and/or intense light irradiation, the catalyzed reaction could proceed very fastly and this could be useful for example in the case of kinetic competition with a (non-catalyzed) parasite reaction, a quite common situation in organic chemistry.

While many problems may arise in this approach mainly due to the delicate surface chemistry of SiNPs, the ever increasing degree of understanding of the chemistry and photochemistry of these remarkable systems might certainly lead to successful applications in the field of light induced redox processes. Currently in our laboratory a careful investigation of diffusional redox processes in solution involving SiNPs is underway and is giving promising results.

## 1.7 Conclusions

As we have shown in this introduction, nanoparticles constitute a fascinating realm at the boundary between the two extensively studied fields of molecular systems and solid state materials, combining properties of both of them, such as the discrete energy levels and localization of charges typical of molecules with the chemical and photochemical robustness of bulk materials.

This unique combination makes them suitable for a large range of applications and fosters the interest for the understanding of their basic properties, to "fill the gap" between the molecule and the bulk solid in terms of the description and understanding of the optoelectronic properties of materials, forcing a convergence between fields that have traditionally "spoken a different language" and thus inducing researchers, whatever is their expertise, to think "out of the box".

A particular application in which they are playing an ever increasing role is that of energy applications, such as solar energy conversion, a field that is central to current scientific research due to the environmental concerns arising from the utilization of fossil fuels.

The ever increasing degree of control over the synthetic procedures to produce nanoparticles and understanding of their chemical reactivity has lead to the creation of hybrid systems in which they are linked to molecular and biomolecular species, enormously increasing the possibility to create combinations of desired properties.

In the field of artificial photosynthesis, in which molecules offer an unrivalled level of control over the fine structural and energetic requirements but suffer from inherent sensitivity to degradation (thus limiting their value for real life applications), nanomaterials and their hybrids have been proven to perform excellently when appropriately designed, giving new hopes to a field that despite its solid theoretical understanding and enormous potential utility, has been struggling for a long time to make the final step to the real application.

Among all the materials that have been prepared in form of nanoparticles, silicon presents several intriguing properties such as its abundance, low cost and non-toxicity, together with peculiar optoelectronic properties arising from the indirect nature of its band gap (such as a very long exciton lifetime). Moreover silicon, being immediately under carbon in the periodic table, presents a rich covalent chemistry that would be impossible to perform on the ionic compounds that constitute the majority of the other reported quantum dots, allowing for a robust integration with organic materials and wide tunability of properties through surface functionalization.

In this thesis work, we will present a case of integration of a conjugated oligomer with silicon nanoparticles, to explore new hybrids in the field of light harvesting and nonlinear optics, together with the synthesis of a class of molecules that have been designed with the aim of integrating them with silicon nanoparticles, to realize systems capable of performing energy transfer processes and drive the formation of supramolecular aggregates upon chemical stimuli.

In the last chapter we will employ a different type of nanoparticle, a platinum one, to realize a supramolecular hybrid with a photoactive dendrimeric material, a novel approach in the design of systems capable of coupling light absorption, charge separation and catalysis for hydrogen evolution.

## Chapter 2

# A two-photon absorbing organic-inorganic antenna based on silicon nanoparticles

## 2.1 Introduction

As shown in the introductory chapter, our group has recently focused its interest on the design of organic-inorganic light harvesting antennas based on silicon nanoparticles, with the aim to overcome one of the main drawbacks of SiNPs, their poor absorption efficiency due to the indirect-band gap nature of the electronic transition.

Here we expand this approach to the two-photon case. Direct band gap quantum dots show very high two-photon absorption (2PA) cross section values (in the order of  $10^4 \text{ GM}$ )<sup>85–87</sup>. For silicon nanoparticles, the 2PA band shape was reported <sup>88</sup>, with no quantitative "per particle" cross section. In our hands however (see experimental part) they proved to be weak absorbers (< 100 GM at 800 nm) and sensitization of their emission by an efficient two-photon absorber might be a valuable strategy.

Before going into the experimental details, a short overview on the phenomenon of 2PA will be presented together with the design strategies that have been developed to obtain efficient two-photon absorbers, with a focus on the type of chromophores that will be used in this work (thiophene-benzothiadiazole-thiophene D-A-D oligomers). Furthermore, we'll describe the utility of 2PA probes in one of their many applications, two-photon microscopy, chosen due to the promising properties of quantum dots in the field of bioimaging.

<sup>&</sup>lt;sup>85</sup>Pu, S.-C. et al. (2006).  $\overline{Small \ 2, \ 130}$ 8–1313.

<sup>&</sup>lt;sup>86</sup>He, G. S. et al. (2007). Optics express 15, 12818–12833.

<sup>&</sup>lt;sup>87</sup>Larson, D. R. et al. (2003). *Science 300*, 1434–1436.

<sup>&</sup>lt;sup>88</sup>He, G. S. et al. (2008). Nano letters 8, 2688–2692.

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## 2.1.1 Two-photon absorption

Let's consider a light beam propagating through a material along a direction z, which has an uniform transverse intensity distribution and whose initial intensity is not dependent on time. The attenuation of the light beam due to absorption phenomena in the medium is described by the general law:

$$\frac{dI(z,\lambda)}{dz} = -\alpha(\lambda)I(z,\lambda) - \beta(\lambda)I^2(z,\lambda) - \gamma(\lambda)I^3(z,\lambda) - \eta(\lambda)I^4(z,\lambda)\dots$$
 (2.1)

In the field of linear optics, only the first term is non-negligible, and the integration of the remaining expression leads to the well-known Lambert-Beer law for linear absorption. The other terms are responsible for the phenomena of multi-photon absorption (here we represented in the equation only two, three and four photon processes).

Here we are interested in describing only the 2PA phenomenon and thus we'll truncate the equation to the second term. Moreover, due to the huge diversity in the magnitude of the coefficients  $\alpha(\lambda)$  and  $\beta(\lambda)$ , 1PA will always overcome 2PA at any wavelength at which the material shows linear absorption, leading to the fact that 2PA is observable only for those wavelengths for which  $\alpha=0$ , further simplifying the expression:

$$\frac{dI(z,\lambda)}{dz} = -\beta(\lambda)I^2(z,\lambda)$$
(2.2)

Integration over a distance d gives the function describing the attenuation of light in the medium due to 2PA phenomena:

$$I(d,\lambda) = \frac{I(0,\lambda)}{1 + \beta(\lambda)I(0,\lambda)d}$$
(2.3)

from which the expression for transmittance is easily derived:

$$T(d,\lambda) = \frac{I(d,\lambda)}{I(0,\lambda)} = \frac{1}{1+\beta(\lambda)I(0,\lambda)d}$$
(2.4)

Even though we won't discuss here the different techniques for measuring 2PA and the drawbacks of those relying on transmittance in particular<sup>89,90</sup>, it's important to note that the assumption we made at the beginning (i.e. an uniform transverse intensity and a time-independent  $I(0, \lambda)$ ) don't correspond to the typical experimental conditions, involving focused light and short pulses, and a more complicate treatment should be used. This makes particularly attractive those techniques that rely on the measurement

<sup>&</sup>lt;sup>89</sup>Pawlicki, M. et al. (2009). Angewandte Chemie International Edition 48, 3244–3266.

<sup>&</sup>lt;sup>90</sup>Xu, C. et al. (2015). Cold Spring Harbor Protocols 2015, pdb-top086116.

of 2PA with respect to a reference compound under the same experimental conditions (such as the two-photon excited fluorescence technique used in our study), since the error that would arise automatically cancels out.

The parameter  $\beta(\lambda)$  is a macroscopic quantity (in units of cm/GW), that can be related to molecular parameters by the relation:

$$\beta(\lambda) = \sigma_2'(\lambda) N_0 \tag{2.5}$$

where  $N_0$  is the volume density of molecules (in units of cm<sup>-3</sup>). Though  $\sigma'_2(\lambda)$  is a directly measurable quantity (in units of cm<sup>4</sup>/GW), a parallel expression is more often used:

$$\sigma_2(\lambda) = \sigma_2'(\lambda)h\nu \tag{2.6}$$

where  $h\nu$  is the energy of the photon corresponding to the exciting wavelength. The parameter  $\sigma_2(\lambda)$  (sometimes also called  $\delta$  in literature), defined molecular "two-photon absorption cross section" is the critical parameter describing the capacity of a molecule to participate in a 2PA process. It is in units of cm<sup>4</sup> photon<sup>-1</sup> s (or simply cm<sup>4</sup> s), but since most of the measured systems lay in the interval 10<sup>-51</sup>-10<sup>-46</sup> cm<sup>4</sup> s, an informal unit, the GM (the name abbreviation of Maria Göppert-Mayer, who provided the first theoretical prediction of 2P phenomena in 1931) is usually employed:

$$1GM = 10^{-50} cm^4 s \tag{2.7}$$

Before going into details into the parameters that define  $\sigma_2$ , we need to give a physical description of the phenomenon of multi-photon absorption and in particular on the key concept of "virtual state"<sup>91</sup> (sometimes defined more meaningfully as "intermediate state"; however we will not use this terminology here to avoid confusion in the sum-over-states expression described below).

The phenomenon of 2PA (and by extension all the multi-photon processes) can be visualized as a "two-step" event (*Figure 2.1*), in which a photon is firstly absorbed by a molecule in its ground state to populate a virtual state, then a second photon will induce the second transition from the virtual to the final state. In the virtual state, the molecular status is not certain, in the sense that the molecule is in a superimposition of all its possible eigenstates (except the ground and final states) with a certain distribution probability. Because the uncertainty on the distribution range is very large, the residence time of the molecule in the virtual state is extremely short, and the absorption of the two photons should be regarded as simultaneous (clearly distinguishing 2PA from the

<sup>&</sup>lt;sup>91</sup>He, G. S. et al. (2008). *Chemical Reviews 108*, 1245–1330.

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Figure 2.1: A schematic representation of the phenomena of two, three and four photon absorption. Note that here the notation "intermediate state" is used for what is called "virtual state" in the text. (Reprinted with permission from ref. (91))

phenomenon of excited state absorption).

With this idea of virtual state in mind, we can better understand the following equation, in which  $\sigma_2$  is expressed as function of the light frequency  $\nu$ :

$$\sigma_2(\nu) = \frac{2\pi h\nu^2 L^4}{\varepsilon_0^2 n^2 c^2} \left(\frac{1}{\Gamma}\right) \underbrace{\left[\sum_i \frac{\langle \vec{\mu}_{gi} \vec{\mu}_{if} \rangle}{(E_{gi} - h\nu)}\right]^2}_{S_{fg}}$$
(2.8)

where  $\varepsilon_0$  is the vacuum permittivity, n is the solvent refractive index, c is the speed of light and  $\Gamma$  is the half-width at half maximum of the 2PA band in energy units. The factor  $L = (n^2 + 2)/3$  represents the enhancement of the optical field in the medium with respect to the vacuum.

The part of the equation bearing the most of information on the molecular properties is however  $S_{fg}$ , the so-called "sum-over-states" (SOS) expression, that describes the transition from the ground to the final state as a sum of contributions that take into consideration the transition vectors from the ground to an intermediate state and from that intermediate to the final state. It's important to note that the intermediate state is not what we previously called the virtual state, but it is a real eigenstate of the molecule. The sum runs on every eigenstate except the ground and final state and each of the terms of the sum actually measures the contribution of the particular eigenstate i to the virtual state, that is dependent upon the difference between its energy  $(E_{gi})$ and that of the virtual state (which corresponds to the energy of the photon  $h\nu$ ).

The transition dipole moments  $\vec{\mu}_{gi}$  and  $\vec{\mu}_{if}$  rotate in solution with the molecules, so their average should be made onto the direction of the optical field (this is the meaning of the pointed brackets in equation 2.8). If the moments are coparallel (this is true for the great majority of strong 2P absorbers), the result is 1/5, and the expression becomes:

$$S_{fg} = \frac{1}{5} \underbrace{\left(\frac{\Delta \mu_{gf} \mu_{gf}}{h\nu}\right)^{2}}_{D} + \frac{1}{5} \underbrace{\sum_{i \neq f,g} \left(\frac{\mu_{gi}^{2} \mu_{if}^{2}}{(E_{gi} - h\nu)^{2}}\right)}_{T}$$
(2.9)

where D can be defined as the "dipolar" term and T as the "two-photon" term.

To describe the importance of this two factors for different molecular structures, we will examine two cases: centrosymmetric (quadrupolar) molecules and dipolar ones. Other cases, such as octupolar, dendrimeric or polymeric architectures are important and investigated in literature<sup>89,91,92</sup>, but since those two are sufficient to describe the photophysics of our system we will focus our attention only on them.



Figure 2.2: A schematic representation of two photon absorption for centrosymmetric and dipolar chromophores. (Reprinted with permission from ref. (89))

In centrosymmetric chromophores, all static dipole moments are zero, and thus the D term is absent. A simplified model can be used to qualitatively understand their 2PA properties, in which only one intermediate state is taken into consideration (three states model).

The origin and significance of the three states will be treated more in detail in the experimental section. For now, we will limit our explanation to the fact that, due to symmetry considerations, the ground to intermediate state and intermediate to final state transitions are one-photon allowed and two-photon forbidden, while the reverse is valid for the ground to final state transition.

The intensity of the transition would depend on the contribution of the one-photon allowed intermediate state to the virtual state, and thus the smallest is the difference  $\Delta = E_{gi} - h\nu$ , the most intense the 2P transition will be.

Viceversa, in dipolar molecules T term makes a smaller contribution (because the intermediate states, and the D term is the dominant term, since the transition from the

<sup>&</sup>lt;sup>92</sup>Mongin, O. et al. (2006). Chemical communications 8, 915–917.

ground to the final state is both 1P and 2P allowed. The intermediate state lays above the final state in energy, and  $\Delta$  is very high, thus strongly decreasing the importance of the T term.

Comparing the two systems, due to the effect of the denominators in equation 2.9, the T term in centrosymmetric chromophores is higher than the D term in analogous (i.e. composed by the same donor-bridge-acceptor units) dipolar dyes, and this explains in part the better 2PA properties of the former.

Moreover, centrosymmetric chromophores allow the charge to be displaced in both directions with respect to the D-A-D axis. In this way, the charge diplacement occurs in both parts of the optical cycle (taking the interval of a sinusoidal wave between two successive maxima, the polarization happens both when the amplitude is positive and when it is negative, while for dipolar molecules it happens in just one of the cases, depending on the orientation of the molecule with respect to the direction of propagation of the wave), making  $\mu_{gi}$  in D-A-D system larger than  $\mu_{gf}$  in the corresponding D-A analogue.

In general, without entering in the detail, that can be found elsewhere<sup>89,93</sup>, a few rules can be applied to the design of efficient 2PA chromophores:

- Centrosymmetric chromophores that possess strong 1PA bands near in energy to the half of the energy of the 2P allowed state have a little Δ value and consequently a large T term;
- Long  $\pi$ -conjugated systems with enforced coplanarity lead to large values of the transition dipole moments, enhancing both the D and the T term;
- Increasing the strength of the donor and acceptor groups lead to the same result;
- Sharp 1PA and 2PA bands are to be preferred due to the reduction of the Γ value in equation 2.8;

## 2.1.2 Two-photon microscopy

Traditional 1PA-based microscopy techniques are limited in use to a region of less than 100  $\mu$ m depth from the tissue surface due to scattering phenomena that significantly blur the image, leading to a strong loss of resolution. The exploitation of 2PA processes, with the development of the so-called "two-photon excited microscopy" has lead to a rapidly expanding field of imaging studies in intact tissues and living animals at depth of up to 1 mm<sup>94</sup>.

<sup>&</sup>lt;sup>93</sup>Strehmel, B. et al. (2003). ChemPhysChem 4, 249–259.

<sup>&</sup>lt;sup>94</sup>Helmchen, F. et al. (2005). Nature methods 2, 932–940.

In fact, this technique is inherently less affected by scattering for at least two reasons:

- The excitation wavelength is usually located in the NIR region, where scattering is less efficient and light penetrates better the tissues due to low absorption from the biological environment (the so called "biological spectral window")
- The strong power intensity required for 2PA is reached only in a very narrow spot on the focal plane (leading to high-resolution imaging in 3 dimensions), and even in a strongly scattering medium, the intensity of the scattered light will never be strong enough to generate a 2PA phenomenon.



Figure 2.3: A cuvette containing a solution of fluorescein, showing the difference in the excitation volume between one-photon confocal microscopy (left) and two-photon microscopy (right). Image by Steve Ruzin and Holly Aaron, UC Berkeley.

Due to these advantages, combined with the fact that the background signal from the biological matrix is very low due to the very poor cross sections (less than 1 GM) of biologically relevant emitters<sup>90</sup>, has stimulated researchers to design two-photon probes for a variety of analytes<sup>95,96</sup>.

In the field of optical imaging, an interesting alternative to molecular dyes is represented by quantum dots<sup>97</sup> due to their high brightness, chemical and photochemical robustness, long lifetimes and wide tunability. In the field of 2P imaging, direct-band gap quantum dots have shown very promising properties due to their excellent 2PA cross sections<sup>87</sup>.

As already stated at the begging of this introduction, this is not the case for indirect band-gap quantum dots, such as the silicon ones employed in this study, and sensitization of their emission with two-photon absorbing organic molecules will be attempted to investigate the possibility of efficient use of SiNPs in 2P applications.

<sup>&</sup>lt;sup>95</sup>Kim, D. et al. (2014). Organic & Biomolecular Chemistry 12, 4550–4566.

<sup>&</sup>lt;sup>96</sup>Guo, L. et al. (2014). Advanced Materials 26, 5400–5428.

 $<sup>^{97}\</sup>mathrm{Resch-Genger},$  U. et al. (2008). Nature methods 5, 763–775.

## 2.1.3 Thiophene-benzothiadiazole-thiophene oligomers for 2PA

The 2PA dye used in this study (named THP hereafter) was synthesized by the group of Prof. Yuguo Ma at the Peking University (China) and chosen due to the promising properties of related compounds reported in literature.



Figure 2.4: The THP chromophore employed in this study as 2P sensitizer for SiNPs.

In a recent work by the group of Reynolds<sup>98</sup> a family of  $\pi$ -conjugated oligomers based on thiophene donors and different acceptor units were studied for application in optoelectronics and non-linear optics. Among them, the three compounds shown in *Figure 2.5* together with their 1P and 2P absorption spectra have shown promising two photon cross section values of about 2500 GM at 700 nm, in accordance to what reported in another study by the group of Mataka on a similar compound<sup>99</sup> (1300 GM at 700 nm).



Figure 2.5: The three thiophene-benzothiadiazole-thiophene oligomers reported in the study by the group of Reynolds (a) and their 1P and 2P absorption spectra (b). Reprinted with permission from ref. (98).

In all cases however, the large conjugation system shifts the photophysical properties of the compounds too much towards the red to be applied for SiNP sensitization (see

<sup>&</sup>lt;sup>98</sup>Ellinger, S. et al. (2011). Chemistry of Materials 23, 3805–3817.

<sup>&</sup>lt;sup>99</sup>Kato, S.-i. et al. (2006). Chemistry–A European Journal 12, 2303–2317.

discussion in the experimental part) and a smaller analogue should be preferred, despite the fact that this may lead to a decrease in the 2PA cross section.

## 2.2 Synthesis of SiNP-THP

The syntesis and functionalization of the SiNPs studied in this work were performed in the group of Prof. Brian Korgel at University of Austin (Texas) by Dr. Mirko Locritani (University of Bologna) and others following the method developed by Hessel<sup>14</sup>.

SiNPs of two different diameters (2.5 and 5.0 nm) were prepared and functionalized with a ligand layer of 1-dodecene and THP to yield the SiNP-THP composites (Figure 1). SiNPs passivated with only 1-dodecene were also prepared as reference for the evaluation of the photophysical properties of the assemblies.



Figure 2.6: Schematic representation of the synthetic procedure used for the production of the SiNP-THP and SiNP-alkyl composites.

40 mL of Fox-16 (hydrogen silsesquioxane 16 wt%) was dried under vacuum and the resulting white solid was then transferred to a tube furnace kept under reducing atmosphere (93% N<sub>2</sub>, 7% H<sub>2</sub>), heated to the desired temperature (1100 °C for 3.0 nm SiNPs or 1200 °C for 5.0 nm SiNPs) with an heating rate of 18 °C/min and held at that temperature for an hour for annealing.

After cooling to room temperature, the obtained  $SiNP/SiO_2$  composite was mechanically ground with a mortar and pestle to obtain a fine powder. To further reduce the grain size to about 200 nm, a wrist action shaker with 30 g of 3 mm borosilicate glass beads was used (until the coarseness of the powder, deducible from its color, appeared not to change any more).

The obtained SiNP/SiO<sub>2</sub> composite was etched with 48% HF and 37.5% HCl (10:1 v/v) in the dark for 4-6 hours and then centrifuged at 8000 rpm for 5 min. The

H-terminated SiNPs were then rinsed once with deionized water, twice with ethanol and once with chloroform.

The nanocrystals were dispersed in 4 mL of 1-dodecene to have alkyl terminated SiNPs (hereafter simply indicated as SiNPs) or in a solution of 70 mg of THP in 4 mL of 1-dodecene (1:120 THP:dodecene molar ratio) for SiNPs-THP. The initially turbid dispersions were degassed with three freeze-pump-thaw cycles and then heated to 170 °C under N<sub>2</sub> flow for 12 hours. Over time, the dispersions became optically clear, indicating that the passivation of Si nanocrystals, which makes them soluble in dodecene, had occurred.

To purify the nanocrystals, the solutions were centrifuged at 8000 rpm for 5 min to and the precipitate (poorly capped SiNPs) was discarded. The supernatant was collected and further purified by several cycles of precipitation and centrifugation using toluene/ethanol solvent/antisolvent pair, until the surnatant appeared clear and nonemissive under UV irradiation. The final SiNP samples were dispersed in toluene at a concentration of 3-5 mg/mL and stored as solutions.

## 2.3 Photophysics of THP

The THP chromophore presents peculiar photophysical properties, related to its solvatochromic properties. In fact, as it is shown in *Figure 2.7*, the absorption spectra are essentially uninfluenced by the polarity of the solvent, while the emission spectra show a strong positive solvatochromism (i.e. the emission is redshifted in more polar solvents), with a big change already in low polarity solvents.



Figure 2.7: Normalized absorption (a) and emission (b) spectra of THP in different solvents.
As a first approach, one should try to separate non-specific solvent interactions (due to the polarizability properties of the solvent) from specific ones (due to specific interactions such as H-bonding or  $\pi$ -stacking). To do that, the Lippert-Mataga formalism<sup>100-102</sup> can be used, in which the molecule is described as a dipole immersed in a dielectric medium, and the main solvent parameters taken in consideration are the refractive index (n) and the dielectric constant ( $\epsilon$ ).

The dependence of the Stokes shift (the difference between the absorption maximum  $\tilde{\nu}_A$  and the fluorescence emission maximum  $\tilde{\nu}_F$  in wavenumber units) from the solvent and molecular properties is described by the equation:

$$\tilde{\nu}_A - \tilde{\nu}_F = \frac{2}{hc} \left( \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right) \frac{\left(\mu_E - \mu_G\right)^2}{a^3} + const.$$
(2.10)

In which the solvent dependent part is described by the "orientation polarizability" parameter  $\Delta f$ , defined as the difference between the "low frequency polarizability"  $f(\epsilon)$ , related to the electronic and nuclear rearrangement of the solvent following the excited state relaxation to its minimum energy geometry, and the "high frequency polarizability" f(n), related to the (relatively) istantaneous movement of the electrons of the solvent during the molecule excitation:

$$\Delta f = \underbrace{\frac{\epsilon - 1}{2\epsilon + 1}}_{f(\epsilon)} - \underbrace{\frac{n^2 - 1}{2n^2 + 1}}_{f(n)}$$
(2.11)

The equation can thus be rewritten as:

$$\tilde{\nu}_A - \tilde{\nu}_F = \frac{2\Delta f}{hca^3} \left(\mu_E - \mu_G\right)^2 + const.$$
(2.12)

In which *a* is the radius of the spherical cavity containing the molecule. The spherical shape is an approximation, and introduces an error for elongated molecules (such as THP), but this doesn't affect substantially the accuracy of the model for our qualitative evaluation purposes.

The most important molecule-related term is actually the difference of the two static dipole moments  $\mu_E - \mu_G$ , referred respectively to the geometry relaxed excited and ground states. It is important to note that taking simply their difference is due to the assumption that  $\mu_E$  and  $\mu_G$  point in the same direction, that can be considered essentially true for many chromophores<sup>103</sup>.

<sup>&</sup>lt;sup>100</sup>Lippert, E. (1955). Zeitschrift für Naturforschung A 10, 541–545.

<sup>&</sup>lt;sup>101</sup>Mataga, N. et al. (1955). Bulletin of the Chemical Society of Japan 28, 690–691.

<sup>&</sup>lt;sup>102</sup>Mataga, N. et al. (1956). Bulletin of the Chemical Society of Japan 29, 465–470.

<sup>&</sup>lt;sup>103</sup>Lakowicz, J. R., Principles of fluorescence spectroscopy, 2013.

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The key point in using the Lippert-Mataga treatment is that in the case of nonspecific solvent interactions the solvent effect on the difference of the static dipoles is minor and the relation between the Stokes shift and  $\Delta f$  is linear. A deviation from the linearity indicates either a specific solvent interaction or an internal charge transfer (ICT) process that induces a strong polarization of the excited state with respect to the ground state.

To evaluate the Stokes shift we have converted the absorption and emission spectra, recorded in wavelength units, into wavenumber units. To do so, not only the X scale must be converted, but also the intensity values should be treated to take into account the principle of conservation of energy<sup>104</sup>, that can be expressed as:

$$I(\tilde{\nu})d\tilde{\nu} = I(\lambda)d\lambda \tag{2.13}$$

By using the relation between wavelength and wavenumber, one obtains:

$$I(\tilde{\nu}) = I(\lambda) \frac{d\lambda}{d\tilde{\nu}} = I(\lambda) \frac{d}{d\tilde{\nu}} \left(\frac{1}{\tilde{\nu}}\right) = -I(\lambda) \frac{1}{\tilde{\nu}^2}$$
(2.14)

where the minus sign is only an indication of the inverse direction of the integral (i.e. of the fact that wavenumber decreases with increasing wavelength and viceversa) and can be ignored.



Figure 2.8: Normalized absorption (a) and emission (b) spectra of THP in different solvents in wavenumber units.

Applying the treatment to the data collected for THP in different solvents results in the plot shown in *Figure 2.9(a)*, while in *Figure 2.9(b)* is shown the dependence of the

<sup>&</sup>lt;sup>104</sup>Mooney, J. et al. (2013). The Journal of Physical Chemistry Letters 4, 3316–3318.

fluorescence emission maximum (the key relevant parameter in this case since there is no appreciable shift in absorption).



Figure 2.9: Absorption (a) and emission (b) spectra of THP in different solvents and the dependence of Stokes shift (c) and emission maximum (d) on the solvent orientation polarizability.

To gain a deeper insight on the effect of solvents on the photophysical properties, fluorescence quantum yields and excited state lifetimes were measured, and the radiative and non-radiative constants derived following the relations:

$$\Phi_{fluo} = k_r \tau = \frac{k_r}{k_r + k_{nr}} \tag{2.15}$$

where  $\Phi_{fluo}$  is the fluorescence quantum yield,  $k_r$  is the radiative constant and  $\tau$  is the excited state lifetime and  $k_{nr}$  is the non-radiative constant.

The plots showing the dependence of the four parameters upon the solvent orientation polarizability are shown in *Figure 2.10*.

First of all, one should notice that the data appear quite scattered due to experimental error, to the choice of the values of refractive index and dielectric constant (for uniformity, solvent properties were all taken from the "CRC Handbook of Chemistry and Physics, 96<sup>th</sup> Edition" and reported in the Appendix section) and to specific solvent effects.

From the lifetime data it appears immediately a strong decrease of the value in protic solvents, confirmed by an increase in non-radiative decay constants, a clear sign of H-bond interactions. DMSO, by minor extent, shows the same effect, possibly due to its high water content. A clear outlier with respect to all the other data is represented by dioxane, but we don't have an explanation for that.

Besides these specific solvent effects, before discussing in more detail the non-specific effects, it is useful to describe the general solvatochromic behaviour of THP, moving from the simple observation of the negligible effect of the solvent on the absorption



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Figure 2.10: The dependence upon the solvent orientation polarizability of the fluorescence quantum yield (a), excited state lifetime (b), radiative constant (c) and non-radiative constant (d) for THP.

properties combined with a strong effect in emission, a clear fingerprint of a charge rearrangement effect (ICT) happening in the excited state.

This effect can be understood in the framework of the theory developed by Terenziani and Blanchard-Desce relating symmetry breaking and solvatochromism for quadrupolar<sup>105</sup> and asymmetric quadrupolar<sup>106</sup> chromophores. Since the latter case is basically an extension of the general theory developed for the former, we will discuss the case of symmetric quadrupolar donor-acceptor-donor (D-A-D) chromophores (corresponding to the thiophene-benzothiadiazole-thiophene backbone in THP) and finally add the specific contribution of the asymmetry (the alkoxyphenyl ring in THP).

The electronic structure of a quadrupolar chromophore can be described as a resonance structure between a neutral and two equivalent (and thus degenerate) zwitterionic structures:

<sup>&</sup>lt;sup>105</sup>Terenziani, F. et al. (2006). Journal of the American Chemical Society 128, 15742–15755.

<sup>&</sup>lt;sup>106</sup>Katan, C. et al. (2010). The Journal of Physical Chemistry B 114, 3152–3169.

$$\underbrace{D^+ - A^- - D}_{|Z_1\rangle} \longleftrightarrow \underbrace{D - A - D}_{|N\rangle} \longleftrightarrow \underbrace{D - A^- - D^+}_{|Z_2\rangle}$$

The combination of the zwitterionic configurations exploiting the centrosymmetric symmetry of the system produces 2 states, a symmetric and an antisymmetric one:

$$|Z_{+}\rangle = \frac{1}{\sqrt{2}} (|Z_{1}\rangle + |Z_{2}\rangle)$$
$$|Z_{-}\rangle = \frac{1}{\sqrt{2}} (|Z_{1}\rangle - |Z_{2}\rangle)$$

The mixing of the symmetric  $|Z_+\rangle$  and  $|N\rangle$  states gives rise to the three states that define the system, the ground state  $|g\rangle$ , the intermediate state  $|i\rangle$  and the final state  $|f\rangle$ :

$$\begin{split} |g\rangle &= \sqrt{1-\rho} |N\rangle + \sqrt{\rho} |Z_+\rangle \\ |i\rangle &= |Z_-\rangle \\ |f\rangle &= \sqrt{\rho} |N\rangle - \sqrt{1-\rho} |Z_+\rangle \end{split}$$

The transition between ground and intermediate state is one-photon allowed and two-photon forbidden, while the reverse is valid for the transition from the ground to final state.

The parameter  $\rho$  depends on the probability of electron transfer from D to A (and backwards) and on the energy difference between  $|N\rangle$  and the degenerate states  $|Z_1\rangle$  and  $|Z_2\rangle$  and determines the charge distribution of the ground state:

$$D^{+0.5\rho} - A^{-\rho} - D^{+0.5\rho}$$

Depending on the value of  $\rho$  and on the degree of vibronic coupling in the molecule, the intermediate state can have a minimum at the ground state minimum energy geometry or a double minimum at two equivalent distorted geometry (plus a third case with a double minimum ground state never reported in real systems), as shown in the diagram in *Figure 2.11(a)*, defining two classes of chromophores.

In both cases, including solvent effects in the relaxation energy from the vertically excited intermediate state to its minimum energy a further deviation from the ground state minimum geometry is obtained, as shown in *Figure 2.11(b)*. This results in a little solvatochromic effect both in absorption and emission for compounds of class II, while it has a much more pronounced effect on class I compounds.

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Figure 2.11: (a) The diagram showing the three possible classes of quadrupolar chromophores reported in the study by Terenziani and Blanchard-Desce. (b) The effect of the solvent polarity on the intermediate state potential energy surface for class I (left) and class II (right) compounds (Images reprinted with permission from ref. (105)).

In this type of chromophores the vertical excitation occurs with no net dipolar charge displacement (i.e. there is a simultaneous transfer of charge from the two peripheral D units to the central acceptor) and thus it is practically not affected by solvent effects, resulting in an absence of solvatochromic effects in absorption.

The presence of the double minimum however causes a localization of the charge on one of the two equivalent arms of the D-A-D structure upon relaxation, resulting in a dipolar structure and a consequent strong solvatochromic behaviour in emission, observable already for low polarity solvents.

In particular, for a compound representative of class I chromophores reported in the study (*Figure 2.12*), a change in the linear slope of the graph reporting the dependance of the emission maximum on the solvent orientation polarizability was observed and attributed to the phenomenon of "false symmetry breaking". In very low polarity solvent in fact, the energy barrier between the two minima is low (see *Figure 2.11(b)*) and a fast tunneling effect produces an overall non-polar state, while upon increasing the polarity a "true symmetry breaking" causes the described polarization of the state.

A more accurate description of the properties of THP may come from the expansion of this original study, in which the same authors investigated the effect of a slight asymmetrization on the electronic properties of quadrupolar compounds <sup>106</sup>. Through the combined experimental and theoretical analysis of three strongly related molecules (*Figure 2.13*) they showed that the slightly asymmetric derivative displayed a very weak positive solvatochromism in absorption (thus substantially retaining the quadrupolar nature of the symmetric analogues), while the emission properties were identical to



Figure 2.12: Absorption and emission properties (b) and the dependence of the emission maximum upon the solvent orientation polarizability (c) for the class I compound (a) reported in the study by Terenziani and Blanchard-Desce (Reprinted with permission from ref. (105)).

those of the symmetric analogue bearing the most electron-donating alkyl amine groups (Q1 in *Figure 2.13*), demonstrating that the charge localizes on the arm of the D-A-D structure bearing the strongest donor group. Notably, in this case no change of the slope in the Lippert-Mataga plot was observed and this was attributed by the authors to an easier polarization already in very apolar solvents.



Figure 2.13: The three related compounds investigated by Terenziani and Blanchard-Desce to prove the effect of asymmetry in quadrupolar dyes (Reprinted with permission from ref. (106)).

Based on the analogy between the structure of THP and that of the model compounds described in the theoretical framework presented above, we think that the same effect may be responsible for the photophysical properties of our system. However, in our case it is hard to distinguish if we can observe a double regime in the Lippert-Mataga plot. In fact, the dependence of Stokes shift and emission maximum on the solvent polarizability seems to effectively show a deviation from the linearity passing from the region "hexane-diethyl ether" to the region "dichloromethane-methanol" and this appears to be confirmed by the quantum yields trend, but other data that should be indicative of a change in the type of transition, such as radiative constants, appear to be more continuously changing over the entire solvent range.

In conclusion, the relatively high uncertainty on the data doesn't allow to elucidate with absolute certainty this aspect. A considerable help in addressing this issue may come from computational modelling, but the excited state optimization (and in particular the vibrational analysis needed to confirm the convergence to a true minimum) required to confirm the symmetry breaking and charge localization is too computationally intensive for our limited hardware resources.

What is most interesting for our purposes is that this type of chromophores exhibits good two photon absorption (2PA) properties due to the low energy gap between the intermediate state and the virtual state corresponding to half of the energy of the final state. Actually, due to this specific reason, class II chromophores should outperform class I ones in cross section values, but one should take in consideration that a too narrow gap between one-photon and two-photon excitation frequency results inevitably in a limited 2P excitable spectral range (2PA, due to the huge difference in transition probability, can be observed only in regions where the chromophore is transparent with respect to 1P excitation) and in a spectral superposition of the fluorescence with the exciting laser beam (that may require a time-gating approach for applicative purposes).

The two-photon absorption spectrum for THP was recorded experimentally through fs-TPEF (2P excited fluorescence technique), using rhodamine 6G in EtOH solution as reference compound. In this experiment two solutions of known concentration of the sample and reference are irradiated with a femtosecond pulsed wavelength-tunable Ti:sapphire laser ( $\lambda = 680-1080$  nm, FWHM = 120 fs, f = 80 MHz), and their emission collected under identical experimental conditions. The knowledge of their relative fluorescence quantum yields allows the calculation of the sample cross section using the formula:

$$\sigma_{2,S}(\lambda) = \sigma_{2,R}(\lambda) \frac{\langle F(t) \rangle_S}{\langle F(t) \rangle_R} \frac{c_R}{c_S} \frac{\Phi_R}{\Phi_S} \frac{n_R}{n_S} \frac{\langle P_R(t) \rangle^2}{\langle P_S(t) \rangle^2} \frac{\eta_R}{\eta_S}$$
(2.16)

Where  $\sigma_2$  is the two-photon cross section,  $\langle F(t) \rangle$  is the measured fluorescence signal, c is the concentration,  $\Phi$  is the fluorescence quantum yield, n is the refractive index,  $\langle P(t) \rangle^2$  is the incident laser power and  $\eta$  is the detector collection efficiency.

The two photon absorption spectrum of THP is reported in Figure 2.14, compared

with the one-photon one (whose wavelength scale has been multiplied by 2). It is characterized by two bands, a first one, with an intensity of about 200 GM units, corresponds to the ground to final (two-photon allowed) transition while the low intensity band at 960 nm corresponds to the two-photon forbidden ground to intermediate state in the framework of the three states model.

However, although this model is an useful reference for a qualitative assignment of the bands, the THP structure deviates quite largely from the perfect quadrupolar system for which the theory was developed, and more consistently a sum-over-states (SOS) approach should be used to precisely describe its photophysics (i.e. assuming the contribution of higher excited states as intermediate states).



Figure 2.14: One-photon (red) and two-photon (black) absorption spectra of THP. For comparison, the X scale for 1PA has been multiplied by a factor of 2.

## 2.4 Photophysics of alkyl capped SiNPs

The dodecyl capped SiNPs (simply named SiNPs hereafter) presented in this study were of two different types, based on their dimension:

- Red-emissive 2.5 nm SiNPs (named hereafter 2.5 nm SiNPs)
- NIR-emissive 5 nm SiNPs (named hereafter 5 nm SiNPs)

Typical HR-TEM images and size distribution histograms for the two different families of SiNPs are shown in *Figure 2.15*.

These SiNPs are readily soluble in apolar organic solvents and were charachterized in hexanes solution. The absorption and emission spectra for the two families of nanoparticles are presented in *Figure 2.16*. Chapter 2. A two-photon absorbing organic-inorganic antenna based on silicon nanoparticles



Figure 2.15: HR-TEM images and histograms showing the dimension distribution for 2.5 nm SiNPs (a) and 5 nm SiNPs (b).

The absorption coefficients of the nanoparticles were not measured directly due to the difficulty in measuring the exact concentration of nanoparticle systems in solution, and literature values were used<sup>15</sup> ( $\varepsilon$ =5x10<sup>4</sup> cm<sup>-1</sup> M<sup>-1</sup> at 400 nm for 2.5 nm SiNPs and  $\varepsilon$ =5.3x10<sup>5</sup> cm<sup>-1</sup> M<sup>-1</sup> at 400 nm for 5 nm SiNPs). The emission spectra were found to be largely independent from the excitation wavelength and the quantum yields were found to be respectively 8% for 2.5 nm SiNPs (using Ru[(bpy)<sub>3</sub>]<sup>2+</sup> in H<sub>2</sub>O as reference,  $\Phi = 4$  %) and 50% for 5 nm SiNPs (using HITCI in EtOH as reference,  $\Phi = 30$  %).

The emission lifetimes were found to be nearly monoexponential and in the microsecond regime, accordingly with the indirect nature of the transition, and were strongly dependent on the emission wavelength, as reported in *Table 2.1*, accordingly with what reported in literature<sup>22</sup>:

2.5 nm	$\lambda_{em} \ / \ {f nm}$	550	575	600	625	650	675	700	750	800
SiNP	$ au/\mu {f s}$	34	39	46	52	62	74	84	115	146
$5 \mathrm{nm}$	$\lambda_{em} \ / \ {f nm}$	700	725	750	775	800	850	900	950	1000

Table 2.1: Luminescence lifetimes for 2.5nm and 5 nm SiNPs at different emission wavelengths.

Lifetime decays and the dependence of the emission spectra on the applied initial delay are shown in *Figure 2.17* for 2.5 nm SiNPs.



Figure 2.16: Absorption (a) and emission (b) spectra of 2.5 nm (black) and 5 nm (red) SiNPs.

## 2.5 Energy Transfer in SiNP-THP

The SiNP-THP systems show absorption spectra that are essentially the sum of the spectrum of SiNPs and THP, demonstrating that negligible interactions occurs between the nanoparticles and the dye in the ground state. From the knowledge of the absorption coefficients of the two species it is possible to deconvolute the spectral shapes and extract the average number of THP molecules per nanoparticle, that result to be ca. 2 for 2.5 nm SiNPs and ca. 20 for 5 nm SiNPs.

To evaluate the possibility of sensitization of the nanoparticle emission by energy transfer we have prepared mixtures of SiNPs and THP with the same relative concentrations found in the SiNP-THP samples, than made them isoabsorbing with respect to their covalent analogues (*Figure 2.18*).

Two excitation wavelengths were used to prove the photophysical properties of the assemblies:

- 390 nm. At this wavelength the THP spectrum has a minimum, while the SiNPs have an high value of  $\varepsilon$  for both the 2.5 and 5 nm samples, and we can thus assume that only the NPs are absorbing. In this way we can collect the emission spectra for the covalent and mixed samples and evaluate the relative emission intensity of "free" and THP-bound nanoparticles (for 2.5 nm SiNPs a 50  $\mu$ s delay was applied to eliminate the small contribution of THP fluorescence in the emission spectrum).
- 480 nm (2.5 nm SiNP-THP) or 515 nm (5 nm SiNP-THP). At this wavelengths the SiNPs are essentially non-absorbing, while THP has an elevated absorption coefficient. We can thus assume that all the light is absorbed by THP and we can

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Figure 2.17: Emission decays for 2.5 nm SiNPs at different emission wavelengths (a) and emission spectra recorded for different values of initial delay (b).  $\lambda_{\text{exc}} = 300$  nm.

evaluate the degree of quenching of the THP emission and of sensitization of the NP emission (note that in this last case we must use and isoabsorbing solution of only SiNPs to record the 100% sensitization level).

In both 2.5 nm SiNP-THP and 5 nm SiNP-THP the nanoparticles show a decrease in their emission properties upon binding to THP, and this is confirmed also by direct comparison of the lifetimes at different emission wavelengths (compare *Table 2.2* with *Table 2.1*).

2.5 nm	$\lambda_{em} \ / \ {f nm}$	550	575	600	625	650	675	700	750	800
SiNP-THP	$ au/\mu {f s}$	37	42	47	51	59	69	78	101	123
$5 \mathrm{nm}$	$\lambda_{em} \ / \ {f nm}$	700	725	750	775	800	850	900	950	1000

Table 2.2: Luminescence lifetimes for 2.5nm and 5 nm SiNP-THP at different emission wavelengths.

The (nearly complete) quenching of the THP emission and the sensitization of the NP emission (i.e. the amount of energy transfer) is shown in *Figure 2.19*, in which the spectra of the SiNP-THP samples were corrected based on the degree of quenching of the NP emission previously measured by excitation at 390 nm. In the case of 2.5 nm SiNP-THP, the emission shapes of the nanoparticle and of THP are superimposed over a large spectral interval. To evaluate the THP quenching the observed emission (*Figure 2.19(a)*) was deconvoluted to separate the two contributions, exploiting the fact



Figure 2.18: The absorption spectra of the covalent (black) and mixture (red) systems for 2.5 nm (a) and 5 nm (b) SiNP-THP.

that only THP emits in the most blue-shifted part of the spectrum (i.e. 515 nm). To remove the contribution of THP for evaluating the amount of energy transfer (*Figure* 2.19(b)), a delay of 0.05 ms was applied. Due to the different lifetimes between SiNP and SiNP-THP, this leads to a slight underestimation of the efficiency of the process.

Sample	Quench. SiNP	Quench. THP	Energy transfer
2.5 nm SiNP-THP	35%	88%	33%
5 nm SiNP-THP	40%	95%	80%

Table 2.3: Quenching and energy transfer properties for 2.5 nm and 5 nm SiNP-THP.

Table 2.3 shows the quenching-sensitization properties for the two samples. While the quenching of THP emission is nearly quantitative and comparable in the two cases, the energy transfer efficiency is much higher for 5 nm SiNP-THP than for 2.5 nm SiNP-THP. However in both cases there is a discrepancy between the quenching and sensitization efficiencies.

This finding, together with the quenching of the nanoparticle emission upon binding to THP, suggests that another process occurs and competes with energy transfer. A natural candidate to this role is electron transfer.

To evaluate the possibility of such a process one should know the oxidation and reduction potentials of the species involved. While it is simple to measure those potentials for THP through cyclic voltammetry (see *Figure 2.20*), unfortunately every attempt to measure the redox properties of SiNPs lead to failure.

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Figure 2.19: Above: Quenching of THP emission (a) and sensitization of SiNP emission (b) for 2.5 nm SiNP-THP ( $\lambda_{exc}$ =480 nm). Below: Quenching of THP emission (c) and sensitization of SiNP emission (d) for 5 nm SiNP-THP ( $\lambda_{exc}$ =515 nm).

## 2.6 Two photon sensitization of SiNP-THP

Direct measurement of the 2PA properties of the nanoparticles was possible through adaptation of the TPEF setup described above for THP to the specific conditions required by the long lifetimes of our samples. For this purpose, a Poeckels cell was used to modulate the laser pulse frequency and set a delay of 1  $\mu$ s between successive femtosecond pulses, and the amount of emitted light was measured by integration of lifetime decays taken by a phosphorometer on the whole emission spectrum (i.e. without an emission monochromator).

To take into consideration the different response of the detector, two solutions of SiNPs and the two-photon reference compound (a Pd-benzoporphyrin) were irradiated



Figure 2.20: Cyclic voltammetry of THP in 0.1 M TBAPF<sub>6</sub> dichloromethane solution (v = 1 V/s). Working electrode: glassy carbon; counter electrode: Pt wire; reference electrode: Ag quasi-reference. Ferrocene (Fc/Fc<sup>+</sup> = + 0.395 V vs SCE) was used as internal standard.

by the same one-photon excitation system (a pulsed LED light) and their emission recorded by a detector response corrected instrument and by the phosphorometer we used in the two-photon measurements.

The ratio of the emission intensities (between SiNPs and the reference) taken by the latter was then compared to the one taken by the former to find the correction factor.

Unfortunately, only the 2PA cross section of the 2.5 nm SiNPs could be measured due to the lack of response of our detector system in the NIR interval, where 5 nm SiNPs emit most of their light.

The 2PA spectrum of 2.5 nm SiNP is shown in *Figure 2.21* for the interval in which there was no superimposition between the laser pulse and the detection spectral window (that would have led to false signals). As expected, the cross section is not very high.

Considering the possibility of using THP to sensitize the nanoparticles through two-photon excitation followed by energy transfer, two considerations should be made:

- Since less than two THP molecules per nanoparticle are grafted to 2.5 nm SiNPs and ET is quite inefficient, it makes no sense to test 2P excited sensitization on these samples.
- Even though it wasn't possible to record the full emission of 5 nm SiNPs, it is still possible to record a tail of this emission in the red region, that can be used for a direct comparison between the "free" and THP-functionalized nanoparticles.

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Figure 2.21: Two photon absorption spectrum of 2.5 nm SiNPs in hexane.

To perform the 2P sensitization of 5 nm SiNP experiment, new sample had to be prepared, and their properties measured in toluene solution (same solvent used for the 2P experiment) are reported in *Table 2.4*:

Sample	Quench. SiNP	Quench. THP	Energy transfer
5 nm SiNP-THP	50%	90%	70%

Table 2.4: Quenching and energy transfer properties for 5 nm SiNP-THP in toluene.

Remarkably, considering that in the case of 5 nm SiNPs we have around 20 THP molecules per nanoparticle (ca. 18 for the sample used in 2PA experiments), and that each THP molecule has a cross section value of around 200 GM at 720 nm and transfers its excitation energy to the nanoparticle with an efficiency of about 70%, this simple strategy would lead to an increase of the nanoparticle intrinsic cross section of about 2800 GM, a level that is comparable with intense organic absorbers even assuming that the nanoparticle has a negligible 2P cross section at that wavelength.

Unfortunately, when excitation at 720 nm was tried, the power dependence of the emission intensity showed a nearly linear dependence. This is due to the fact that, even though linear absorption spectra show nearly zero absorption of the 5nm SiNPs at 720 nm, this very low value is sufficient for the very high intensity laser pulse to produce a 1P excitation able to overcome the 2P one, due to the very high difference in transition probability between 1P and 2P processes.

Taking this unexpected drawback in consideration, we switched our attention to the low intensity band at 960 nm, that, far from being ideal for any application, can still give a proof of principle of the feasibility of the approach. Even in this case the power dependence for the reference 5 nm SiNP sample was not exactly quadratic (see figure), implying that some degree of one-photon absorption is occurring also at this wavelength, but not enough to prevent a reliable measurement.



Figure 2.22: Emission intensity decays upon 2P excitation at 960 nm (a) and dependence of the emission intensity upon the incident power (b) for 5 nm SiNP and 5 nm SiNP-THP. The intensities are normalized for the different concentration of the samples.

The measured emission decays and power dependences upon excitation at 960 nm are shown in *Figure 2.22(a)*. Even though as expected the 5 nm SiNP-THP have a shorter lifetime with respect to 5 nm SiNP due to the quenching effects described above, the total integrated intensity shows an increase of a factor of 1.43, showing an overall increase in the two photon action (i.e. the two photon cross section multiplied by the emission quantum yield) even at a wavelength where the efficiency of THP in two-photon absorption is very low.

The two-photon absorption and following energy transfer mechanism is confirmed also by the slight increase of the slope of the power dependence (*Figure 2.22(b)*), a further confirmation of the feasibility of the approach.

## 2.7 Conclusions

In the framework of the work of the group on the preparation of light harvesting antenna systems based on the covalent functionalization of red and NIR emissive silicon nanoparticles, we realized a first example of SiNP-based two-photon antenna in which the good two-photon absorption properties of an organic chromophore were exploited to enhance the cross section of the otherwise poorly absorbing nanoparticles.



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Figure 2.23: Symbolic representation of the processes happening in SiNP-THP antennas. Above: One-photon excited antennas for 2.5 nm (a) and 5 nm (b) SiNP-THP in hexanes. Below: Two-photon excited antenna for 5 nm SiNP-THP in toluene (c). Excitation and emission of light is represented by yellow bolts, while emission quenching processes are represented by black bolts. The reported percentages are not to be intended as absolute, but as relative to an isoabsorbing mixture of the two components.

Even though our system is far from being optimized, some interesting results emerge to guide the development of future systems:

- Excitation interval. It has been shown that at least two problems should be considered in choosing a proper excitation wavelength (i.e. a suitable chromophore): the spectral superimposition of the exciting beam with the nanoparticle emission for 2.5 nm SiNPs (that may limit the working range in real applications) and the residual one-photon absorption for 5 nm SiNPs. The range is thus limited for the region > 800 nm for 2.5 nm SiNPs, while more accurate measurements are needed for assessing a reasonable limit for 5 nm SiNPs, but in this case 1P absorption was demonstrated to be non-negligible as far as at 960 nm. It is important to stress that residual 1P absorption can be detrimental for applications, such as 2P microscopy, that take advantage of the low focal volume in which 2P processes can occur, leading to a loss of resolution. However it has been shown that the 2P to 1P absorption ratio can be incremented through our 2P antenna strategy, possibly making 1P absorption negligible for properly designed antenna systems.
- *Energy and electron transfer*. Both 2.5 nm SiNPs and 5 nm SiNPs were able to nearly completely quench the emission of the THP chromophore (emission in the

500-700 nm range), but the efficiency of energy transfer was found to be way higher for 5 nm SiNPs than for 2.5 nm SiNPs. It is unclear if this results comes from a better energy acceptor ability of larger nanoparticles or from a reduced competition of parasitic processes. In this regard, electron transfer should be regarded as the most probable competitor and might be responsible for both the quenching of the SiNPs emission and the incomplete sensitization upon excitation of THP.

With these guidelines in mind, one could think of what properties the ideal chromophore should possess to be applied as an efficient 2P sensitizer for SiNPs. Besides the obvious advantage of an as-high-as-possible two-photon absorption cross section, the spectral region in which the 2PA peak should fall should be at least >800 nm to be applied on 2.5 nm SiNPs, and far beyond for the 5 nm SiNPs.

While this may lead to think that the realization of an efficient antenna system would be easier for 2.5 nm SiNPs, the fact that energy transfer appears to be less efficient, whether for intrinsic reasons or for an increased competition with electron transfer (that should be very dependent on the dimensions of the nanoparticles given the strong changes of the HOMO and LUMO levels due to quantum confinement) a careful simultaneous optimization of the two-photon, one-photon and redox properties should be performed.

In this regard, the blueshift of the chromophore emission should be regarded as beneficial for the increase of efficiency of energy transfer processes due to the better superposition between the donor emission and the acceptor absorption <sup>107</sup>. This leads to the consideration of the electronic nature of the organic sensitizer. In fact, dipolar dyes have their strongest 2PA band at exactly the double of the wavelength of the  $S_0$ - $S_1$ band in the linear absorption spectrum, while for quadrupolar dyes, generally regarded as better 2P absorbers, this band appears at shortest wavelengths (e.g. 720 nm vs 960 nm for THP).

Moreover, as for now, the very little degree of functionalization of 2.5 nm SiNPs obtained with the employed synthetic method, severely limits the applicability of this type of nanoparticles in antenna systems and further stresses out the importance of significantly improving the synthetic strategy. In fact, due to the complicate requirements for the choice of a good 2PA chromophore, one of the most valuable strategies (provided the elimination of quenching effects of the dye on the nanoparticle emission) remains the simple increase of the number of chromophores on the nanoparticle surface, as clearly demonstrated by the increase in the 2P brightness of 5 nm SiNP-THP even

<sup>&</sup>lt;sup>107</sup>Balzani, V. et al., Photochemistry and photophysics: concepts, research, applications, 2014.

upon excitation on a low-absorbing band in a system with roughly half the emission quantum yield of the reference 5 nm SiNPs.

To conclude, the task of designing a two-photon antenna based on SiNPs is absolutely non-trivial, but it may lead to completely new systems showing a 2P brightness comparable or even superior to the best organic molecules, coupled to unique properties such as excited state lifetimes in the microsecond regime, at room temperature in presence of oxygen. The choice of red or NIR emissive nanoparticles as best acceptors for the antenna system cannot be done a priori, but depends exclusively on the specific application for which the system is designed.

## Chapter 3

# Benzodipyrrins and their metal complexes: exploring new roads in fluorescence

## 3.1 Introduction

#### 3.1.1 Coupling SiNCs to red-NIR emitters

Having the goal to construct organic-inorganic antenna systems composed of silicon nanocrystals and luminescent molecules, we focused our interest on red-NIR emissive species, in order to understand how far we can push the sensitizer emission to the long wavelength part of the spectrum without a significant decrease in the energy transfer efficiency.

In particular, molecules possessing a rigid conjugated backbone, such as cyanines, typically exhibit a very strong  $S_0$ - $S_1$  absorption band in the red-NIR region and fluorescence with high quantum yields and small Stokes shifts. These properties are ideal for the realization of a system able to absorb red-NIR light and transfer the excitation energy to the nanocrystals, which is an important feature in applications such as bioimaging (for deeper tissue penetration of red-NIR light) and solar light harvesting (to increase the working spectral window of a solar device).

The energy transfer efficiency in such a system should be dependent both on the nanoparticle dimensions, that define the band gap energy, and the spectral properties of the dyes. Moreover, the possibility of electron transfer, which is generally dependent on the HOMO and LUMO energies of the sensitizer, should be taken into consideration. Therefore, we were looking for molecules that could be anchored to the silicon surface (without affecting the photoelectrochemical properties) and that would allow tuning of Chapter 3. Benzodipyrrins and their metal complexes: exploring new roads in fluorescence

the HOMO-LUMO gap and orbital energies by way of convenient synthetic modifications.

#### 3.1.2 BODIPYs, dipyrromethenes and benzodipyrromethenes

Boron dipyrromethene dyes (BODIPYs) exhibit great synthetic versatility, combined with excellent photophysical properties and very good stability<sup>108–110</sup>. However the emission of the minimal BODIPY structure, composed of the two pyrroles and possibly bearing some alkyl substituents, which lays around 500 nm, is way too high in energy for our goal.



Figure 3.1: Top: The dipyrromethene scaffold and its relation to the porphyrin structure. Bottom: The BODIPY structure.

Indeed the scientific community has been very actively researching ways to shift the emission to longer wavelengths through synthetic modification of the dipyrromethene (also called dipyrrin) backbone<sup>110,111</sup>. One of the main strategies has been the expansion of the conjugation path through the introduction of  $\alpha$ -substituents, which has been proven very effective<sup>111</sup>.

A less investigated but equally effective approach has been the expansion of the

<sup>&</sup>lt;sup>108</sup>Loudet, A. et al. (2007). Chemical reviews 107, 4891–4932.

<sup>&</sup>lt;sup>109</sup>Ulrich, G. et al. (2008). Angewandte Chemie International Edition 47, 1184–1201.

<sup>&</sup>lt;sup>110</sup>Gómez-Durán, C. F. et al. (2016). Chemistry-A European Journal 22, 1048–1061.

<sup>&</sup>lt;sup>111</sup>Lu, H. et al. (2014). Chemical Society Reviews 43, 4778–4823.



Figure 3.2: An image showing the research effort toward the synthesis of red-emissive BODIPYs (Reprinted with permission from ref. (111)).

pyrrolic units with benzofused rings, leading to benzoBODIPYs<sup>112–115</sup>, naphtoBODIPYs and bigger analogues<sup>111</sup>, due to the higher synthetic complexity of this type of derivatives relative to the preparation of the dipyrromethene backbone, which benefits from the very extensive knowledge developed by chemists on the synthesis of porphyrins through condensation of pyrroles and aldehydes<sup>116</sup>.

In fact, it is the impossibility to apply this type of chemistry to isoindoles (due to their instability) to considerably complicate the situation for benzofused analogues and chemists have developed strategies that involve the formation of the isoindolic structure as a final step, when the presence of a methylene group between the two isoindolic moieties stabilizes the system, putting them in conjugation in the same aromatic backbone (while isoindole itself is antiaromatic). However these strategies

<sup>&</sup>lt;sup>112</sup>Ulrich, G. et al. (2011). The Journal of organic chemistry 76, 4489–4505.

<sup>&</sup>lt;sup>113</sup>Shen, Z. et al. (2004). Chemistry-A European Journal 10, 4853–4871.

<sup>&</sup>lt;sup>114</sup>Tomimori, Y. et al. (2011). Tetrahedron 67, 3187–3193.

<sup>&</sup>lt;sup>115</sup>Wada, M. et al. (2001). *Tetrahedron Letters* 42, 6711–6713.

<sup>&</sup>lt;sup>116</sup>Lindsey, J. S. (2009). Accounts of chemical research 43, 300–311.

usually involve high-temperature synthetic conditions<sup>112,115</sup>.

A notable exception is represented by the synthetic procedures developed by the groups of Cheprakov and Vinogradov<sup>117-119</sup> for the preparation of benzofused porphyrins and dipyrrins, which focus on the use of an easily aromatizable pyrrolic derivative, that allows the application of the well known pyrrole-aldehyde chemistry, followed by oxidation with DDQ (2,3-Dichloro-5,6-dicyano-1,4-benzoquinone).

## 3.1.3 Metal complexes of dipyrrins and benzodipyrrins

Despite the fact of having been employed in supramolecular chemistry <sup>120</sup>, metal complexes of dipyrrins have been seldomly reported as luminescent species in comparison with BODIPYs.

Even though it is not the only metal to generate emissive complexes<sup>121,122</sup>, Zn<sup>2+</sup> has been the most extensively studied and presents the advantage to readily form complexes with tetrahedral geometries upon mixing in solution, leading to the possibility of its application in photofunctional supramolecular materials<sup>123</sup>.

The luminescent properties of Zn-dipyrrins have been shown to depend strongly on the homoleptic or heteroleptic nature of the complex and on the rigidity of the backbone. In a study by Lindsey<sup>124</sup> it has been shown that increasing the steric hindrance on the meso aryl ring, and thus reducing its rotational mobility, highly emissive homoleptic complexes have been obtained in toluene, however a strong decrease in quantum yield has been observed already in the slightly more polar DCM.



Figure 3.3: The effect of increase steric hindrance on the meso aryl ring in enhancing the fluorescence quantum yield of homoleptic Zn-dipyrrin complexes (Reprinted with permission from ref. (124)).

<sup>&</sup>lt;sup>117</sup>Finikova, O. S. et al. (2003). The Journal of organic chemistry 68, 7517–7520.

<sup>&</sup>lt;sup>118</sup>Filatov, M. A. et al. (2007). European journal of organic chemistry 2007, 3468–3475.

<sup>&</sup>lt;sup>119</sup>Filatov, M. A. et al. (2008). J. Org. Chem 73, 4175–4185.

<sup>&</sup>lt;sup>120</sup>Baudron, S. A. (2010). CrystEngComm 12, 2288–2295.

<sup>&</sup>lt;sup>121</sup>Wood, T. E. et al. (2007). Chemical reviews 107, 1831–1861.

<sup>&</sup>lt;sup>122</sup>Baudron, S. A. (2013). Dalton Transactions 42, 7498–7509.

<sup>&</sup>lt;sup>123</sup>Sakamoto, R. et al. (2015). Nature communications 6.

<sup>&</sup>lt;sup>124</sup>Sazanovich, I. V. et al. (2004). Journal of the American Chemical Society 126, 2664–2665.

An explanation of this phenomenon has been proposed by Nishihara<sup>125</sup> that has shown through experimental and theoretical data that the fall of emission intensity with solvent polarity can be explained by the formation of CT states (even though a weakness of this hypothesis is that a direct spectroscopical evidence of the CT states has not been reported) and controlled by the appropriate choice of the dipyrrin ligands in heteroleptic complexes (*Figure 3.4(a)*). In fact, if the frontier orbitals are properly aligned, the charge transfer can be reduced, leading to an increase in the emission quantum yield in DCM with respect to an homoleptic analogue. However, even in this case there was a decrease with respect to toluene and no other solvent was reported.

To the best of our knowledge, nearly all of the reported Zn-dipyrrin complexes are either homoleptic or contained two different dipyrrin ligands. This fact leads to limited possibilities in the tuning of orbital energies and the photophysical properties will be always affected by quenching CT states in polar solvents. A notable exception is represented by an heteroleptic complex recently published by Nishihara<sup>126</sup>, containing bisoxazoline (BOX) as a "large gap" ancillary ligand.

Interestingly, Cheprakov and Vinogradov have demonstrated that benzodipyrrins behave quite differently with respect to their non-benzofused counterpart<sup>127</sup>, with the possibility to form relatively stable heteroleptic complexes with ligands such as acetate, even though it is unclear if this stability is due to the expansion of the pyrrolic rings or to the presence of electron-withdrawing ester substituents in  $\alpha$ -position. Following the hypothesis of Nishihara, in these complexes the narrow HOMO-LUMO gap of the benzodipyrrin ligand, combined with the wide HOMO-LUMO gap of acetate, leads to a strong suppression of the CT states, and the complexes have been shown to be strongly emissive in DMF in the red region, and even in H<sub>2</sub>O<sup>128</sup>.

However, a different explanation is possible. In fact these complexes have a tendency to evolve towards the homoleptic non-emissive species (a tendency that can be controlled by using stronger ligands with respect to acetate, such as acetylacetonate), whose spectral features indicate a dipole-dipole coupling phenomenon between the two ligands. This is favoured by a distortion of the tetrahedral symmetry, with the two ligands deviating from an orthogonal orientation, as shown by X-ray structure and DFT geometry optimization.

This observation is of great importance, since it can offer an alternative explanation with respect to Nishihara's one based on CT states. In fact, in homoleptic complexes exciton coupling would be always much stronger than in heteroleptic ones due to the perfect match in energy between the two dipoles and its role in the photophysics of these

<sup>&</sup>lt;sup>125</sup>Kusaka, S. et al. (2012). Chemistry-An Asian Journal 7, 907–910.

<sup>&</sup>lt;sup>126</sup>Kögel, J. F. et al. (2016). Angewandte Chemie International Edition 55, 1377–1381.

<sup>&</sup>lt;sup>127</sup>Filatov, M. A. et al. (2010). Journal of the American Chemical Society 132, 9552–9554.

<sup>&</sup>lt;sup>128</sup>Thyagarajan, S. et al. In SPIE BiOS, 2011, 79100Z–79100Z.

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Figure 3.4: (a) The family of Zn-dipyrrin complexes investigated by Nishihara (Reprinted with permission from reference (125)) (b) The benzofused Zn-dipyrrin complexes studied by Cheprakov and Vinogradov (Reprinted with permission from reference (127)).

systems should not be ruled out without further investigation (even though absorption spectra of homoleptic dipyrrin complexes don't feature the clear spectroscopic signature observed for benzodipyrrin ones, the effects of vibrations and geometrical distortions either in the ground or in the excited state may lead to a certain degree of coupling between the dipoles).

Zinc complexes of benzodipyrrins look to be ideal for the interaction with SiNCs, since:

- They strongly absorb and emit light in the red region
- The bands position can be tuned by modification of the  $\alpha$ -substituents
- An anchoring group for the SiNPs surface can be easily introduced in the meso position
- The controlled formation of the homoleptic complexes may lead to the formation of supramolecular NP assemblies, and the spectral changes (in a region where SiNCs are essentially non-absorbing) can be used to easily monitor the process

Thanks to a six months stay in the laboratory of Prof. Vinogradov at University of Pennsylvania (UPENN), we synthesized a series of benzofused dipyrromethenes with different  $\alpha$ -substituents, with the aim to study their interaction with SiNPs and to further elucidate the basic properties of this unexplored class of luminescent metal complexes.

## 3.2 Synthesis of benzodipyrrins

The investigated compounds were synthesized according to the previously cited procedure reported by the group of Cheprakov<sup>118</sup>, that can be described as composed of three main goals:

- Synthesis of the pyrrolic precursor
- Synthesis of the dipyrromethane precursor
- Synthesis of the final compounds

This procedure allows for a high degree of synthetic versatility and, even though it requires several synthetic steps, has the advantage that the pyrrolic precursor can be prepared in gram scale and stored in the freezer for subsequent use.



The second step is actually a single reaction that can be performed on the gram scale as well and is the one introducing the meso-substituent, a fundamental part of the molecule that can be used either to further tune the photo- and electrochemical properties or to introduce all sort of "uncoupled" moieties, thus without affecting the electronic structure of the chromophoric unit.

In the third part of the procedure the nature of the  $\alpha$ -substituents is modified with the purpose to tune the electronic properties of the molecule. This type of chemistry is partially known because of its utility in the synthesis of benzoporphyrins, but it is still widely unexplored with respect to its non-benzofused counterpart and may lead to unexpected results, as will be shown in the final part of this chapter.

## 3.2.1 Synthesis of the pyrrolic precursor

This multistep procedure involves the preparation of a tosylated ciclohexadiene through a Diels-Alder reaction between tosylacetylene and 1,3-butadiene, followed by reaction



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with t-butyl isocyanoacetate through Barton-Zard chemistry. The resulting product is basically a pyrrole stabilized by the electron-withdrawing alkoxycarbonyl group, fused to a cyclohexene ring that can be easily aromatized by DDQ under mild conditions.

**Trimethyl(tosylethynyl)silane (2)** In a 500 mL round bottom flask  $21.5 \text{ g} (1.53 \times 10^{-1} \text{ mol}, 1 \text{ eq})$  of AlCl<sub>3</sub> were dispersed in 250 mL of DCM, than 30.8 g  $(1.62 \times 10^{-1} \text{ mol}, 1.06 \text{ eq})$  of TsCl were added and the solution was left to stir until complete dissolution of AlCl<sub>3</sub>. In a 1 L three neck round bottom flask equipped with a thermometer and a dropping funnel 26 g  $(1.62 \times 10^{-1} \text{ mol}, 1.06 \text{ eq})$  of bis(trimethylsilyl)acetylene (1) were dissolved in 150 mL of DCM, and the solution was cooled to -10 °C. The previously prepared solution of AlCl<sub>3</sub> and TsCl was added dropwise while always keeping the temperature at -10 °C (about 15 min). The reaction was left to stir at -10 °C for 20 min, then was allowed to warm to RT and left to stir overnight. The solution was then slowly poured in 150 mL of H<sub>2</sub>O/ice, 200 mL of 20% HCl were added and the biphasic solution left to stir for 15 minutes, then the organic phase was washed 3 times with H<sub>2</sub>O, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated. The solid was recrystallized from boiling hexane and collected by filtration to yield 28 g of product (1.11x10<sup>-1</sup> mol, 73%) as a cream-white solid.

1-(ethynylsulfonyl)-4-methylbenzene (3) In a 1 L three neck round bottom flask equipped with a thermometer and a dropping funnel 28 g ( $1.11 \times 10^{-1}$  mol, 1 eq) of 2 were dissolved in 500 mL of MeOH and the solution was cooled to -10 °C. 300 mL of a H<sub>2</sub>O solution of NaF (6 g,  $1.43 \times 10^{-1}$  mol, 1.28 eq) were added dropwise while keeping temperature below 5 °C (about 15 min). The reaction was left to stir at -10 °C for 20 min, then at RT for 2h. The solution was extracted 3 times with DCM, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated. The solid was recrystallized from 400 mL of boiling h exane<sup>I</sup> and collected by filtration to yield 17 g (9.43x 10<sup>-2</sup> mol, 85%) of product as a cream-white solid.

1-Tosyl-1,4-cyclohexadiene (4) In a thick-walled pressure sealed flask 17 g  $(9.43 \times 10^{-2} \text{ mol}, 1 \text{ eq})$  of **3** were dispersed in 50 mL of butadiene<sup>II</sup> and a catalytic quantity of cathechol was added as radical scavenger. The reaction was left to stir at RT for 1 week<sup>III</sup>, then butadiene was evaporated. The solid was dispersed in 200 mL of boiling hexane and EtOAc was added until complete dissolution. The solution was then cooled with the aid of a dry ice/EtOH bath and the precipitate filtered to obtain 18 g (7.68x10<sup>-2</sup> mol, 80%) of **4** as a white powder.

tert-butyl formylglycinate (6) In a 500 mL round bottom flask 22.1 g ( $1.68 \times 10^{-1}$  mol, 1 eq) of tert-butyl glycinate (5) were dispersed in 120 mL of methyl orthoformate, then 20.35 mL ( $2.11 \times 10^{-1}$  mol, 1.25 eq) of triethylamine were added and the solution was refluxed for 48 h. Methyl orthoformate was evaporated and the resulting solid was dissolved in 150 mL of DCM, washed 3 times with NaHCO<sub>3</sub> in H<sub>2</sub>O (pH 8-9), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated to get 11.54 g ( $7.25 \times 10^{-2}$  mol, 43%) of product as an orange oil.

tert-butyl isocyanoacetate (7) In a 500 mL three neck round bottom flask, equipped with a thermometer and a dropping funnel, dried with heatgun under Ar atmosphere, 11.54 g (7.25x10<sup>-2</sup> mol, 1 eq) of **6** were dissolved in 80 mL of DCM and the solution was cooled to -10 °C, than 25.3 mL ( $1.81x10^{-1}$  mol, 2.5 eq) of triethylamine was added and the mixture was stirred for 5 minutes. A solution of 11.12 g ( $7.25x10^{-2}$  mol, 1 eq) of POCl<sub>3</sub> in 30 mL of DCM was added dropwise (about 1 h) while keeping temperature at -5 °C. The reaction was stirred at 5 °C for 30 min and left to warm to RT for 1.5 h. A solution of 14 g ( $1.01x10^{-1}$  mol, 1.4 eq) of K<sub>2</sub>CO<sub>3</sub> in 80 mL of H<sub>2</sub>O was added dropwise, in portions and under intense stirring, while keeping T around 20 °C, then left to stir for 1 h. 50 mL of H<sub>2</sub>O were then added, the organic phase was washed two times with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated at RT to give a red cloudy oily solution, which was distilled (0.025 mmHg,  $60 \circ C^{IV}$ ) to give 8.19 g ( $5.80x10^{-2}$  mol, 80%) of **7** as a transparent oil.

<sup>&</sup>lt;sup>I</sup>If the solid doesn't dissolve completely in boiling hexane, add EtOAc dropwise until dissolution. <sup>II</sup>Added as a liquid after freezing the gas tank in a freezer.

<sup>&</sup>lt;sup>III</sup>After about 24 h the solid was dissolved, but then a new solid formed and at the end of the reaction an abundant yellowish precipitate was present.

<sup>&</sup>lt;sup>IV</sup>Applying vacuum at RT, the solution will start to boil vigorously, due to the presence of water, since the separation of the phases during extraction was quite difficult.

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**2-tert-butoxycarbonyl-4,7-dihydro-2H-isoindole (8)** In a 1 L three neck round bottom flask, equipped with a thermometer and a dropping funnel, dried with heatgun under Ar atmosphere, 7.36 g ( $6.56 \times 10^{-2}$  mol, 1.3 eq) of tBuOK was dispersed in 300 mL of freshly distilled THF and the solution brought to -5/-10 °C. A solution of 8.19 g ( $5.80 \times 10^{-2}$  mol, 1.15 eq) of **7** in 150 mL of freshly distilled THF was added dropwise and the resulting greenish solution left to stir at -5/-10 °C for 30 min. A solution of 11.82 g ( $5.04 \times 10^{-2}$  mol, 1 eq) of **4** in 150 mL of freshly distilled THF was slowly added dropwise (about 1 drop every 4-5 seconds for about 16 h) under intense stirring, keeping T around -5 °C, then the reaction was stirred at RT for 4h. The formed precipitate was filtered and washed with THF, then the filtrated solution was evaporated, redissolved in 400 mL of DCM, washed 2 times with brine<sup>V</sup>, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated. The crude was then purified by SiO<sub>2</sub> column chromatography (DCM) to yield 5.93 g ( $2.70 \times 10^{-2}$  mol, 53%) of **8** as a white solid<sup>VI</sup>, which should be stored in the freezer.

## 3.2.2 Synthesis of the dipyrromethane precursor



This reaction step employs the classical Lindsey's method<sup>116</sup> for the synthesis of dipyrrins and porphyrins from pyrroles and aldehydes. Thanks to the mild reaction conditions, a wide variety of aldehydes can be employed.

In our case we chose a phenyl ester moiety, since the aryl unit is weakly coupled to the conjugated benzodipyrrin backbone due to its perpendicular orientation (see discussion below) and the ester group allows further functionalization through deprotection and peptidic coupling chemistry.

It is interesting to note that any moiety linked to the backbone through an aryl ring will be electronically decoupled, and since many photoactive molecules have conjugated aromatic structure, it would be possible to synthesize molecules in which two photoactive units are very close but still behave as two separated molecules in a fixed relative orientation.

<sup>&</sup>lt;sup>V</sup>The extraction is difficult because of formation of emulsions. It is strongly recommended to centrifuge the emulsion. This results in perfectly separated phases.

 $<sup>^{\</sup>rm VI}$ The product is detectable on TLC by staining with ninhydrin/MeOH 1% (brown spot).

Moreover, there is the possibility to further tune the photophysical properties of the molecule through the introduction of acetylene units, acting as a bridge between the benzodipyrrin structure and a second conjugated molecule, a strategy that has been explored in the case of porphyrins<sup>129,130</sup> and BODIPYs<sup>131,132</sup>.

#### (4-methoxy carbonyl) arylbis (3-tert-but oxy carbonyl-4, 7-dihydro-2H-iso-2H-

indolyl)methane (9) In 50 mL DCM that was degassed by purging Ar for 20 min, 1 g ( $4.56 \times 10^{-3}$  mol, 2 eq) of 8, 374 mg ( $2.28 \times 10^{-3}$  mol, 1 eq) of 4-carboxymethyl benzaldehyde and 190 mg ( $6.84 \times 10^{-4}$  mol, 0.3 eq) of TBACl were added, followed by 87 mg ( $4.56 \times 10^{-4}$  mol, 0.2 eq) of TsOH to start the reaction. The solution was left to stir at RT under Ar for 24 h, then extracted 3 times with 10% aqueous NaHCO<sub>3</sub>, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated at RT. The crude was purified on a short wide SiO<sub>2</sub> column<sup>VII</sup> (Hex/EtOAc 4:1) to obtain 1.20 g ( $2.05 \times 10^{-3}$  mol, 90%) of the product as a slightly pink<sup>VIII</sup>, foamy solid.

#### 3.2.3 Synthesis of the final compounds



BDP1: i) DDQ, THF, RT, O/N, 90%. BDP2: i) 1. TFA, 20-0 °C, 30 min. 2. CH(OMe)<sub>3</sub>, 0-20 °C, 30 min, 52%. ii) DDQ, THF, reflux, 4h, 82%. BDP3: i) DDQ, THF, RT, O/N, 90%. ii) TFA, RT, 6h, 99%. iii) 1. CDMT, NMM, DMA, 0 °C, 2h. 2. N(Oc)<sub>2</sub>, DMA, 0-20 °C, 20h, 16.5%.

In this last step we decided to synthesize three different derivatives. The ester derivative is simply obtained through aromatization of the dipyrromethane precursor. The formyl derivative has been prepared through decarbonylation-formylation (a procedure well developed for the synthesis of benzoporphyrins) followed by aromatization

<sup>&</sup>lt;sup>129</sup>Anderson, H. et al. (1998). Journal of the Chemical Society, Perkin Transactions 1, 1607–1612. <sup>130</sup>Kuo, M.-C. et al. (2007). Dalton Transactions 14, 1433–1439.

<sup>&</sup>lt;sup>131</sup>Kusaka, S. et al. (2013). Chemistry-An Asian Journal 8, 723-727.

<sup>&</sup>lt;sup>132</sup>Misra, R. et al. (2014). Dalton Transactions 43, 4854–4861.

<sup>&</sup>lt;sup>VII</sup>If it stays too much on  $SiO_2$ , it may degrade.

<sup>&</sup>lt;sup>VIII</sup>The pink color is due to traces of dipyrromethene that forms upon oxidation in air. The product should be stored in freezer.

with DDQ in refluxing THF. The amide derivative was prepared by deprotection of the ester and peptiding coupling between the resulting carboxylic acid and a secondary amine. Admittedly, dioctylamine was used for contingent reasons and it is not the best choice due to its high steric hindrance and insolubility in DMA, resulting in poor yields and unexpected side reactions. In this case, NMR characterization was attempted but gave unclear results due to low concentration and solvent contamination in the aliphatic region. However, MALDI and photophysical measurements clearly show that the product was isolated with a good degree of purity. Further studies are ongoing to synthesise derivatives with shorter alkyl chains and unambiguosly obtain all the necessary data for a complete structural characterization.

#### BDP1



#### (4-methoxy carbonyl) arylbis (3-tert-but oxy carbonyl-isoindolyl) methene

(BDP1) 101 mg (1.73x10<sup>-4</sup> mol, 1 eq) of **9** were dissolved in 15 mL of THF, then 58.2 mg (8.66x10<sup>-4</sup> mol, 5 eq) of DDQ were added, the reaction was refluxed for 2 h and left to stir O/N at RT. The solution was then diluted with DCM and washed 4 times with aqueous Na<sub>2</sub>SO<sub>3</sub> 10%, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated. The crude was purified by on SiO<sub>2</sub> column (DCM/THF 20:1) to obtain 90 mg (1.55x10<sup>-4</sup> mol, 90%) of product as a purple solid<sup>IX</sup>. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>:  $\delta = 14.73$  (s, 1H), 8.34 (d, 2H), 8.13 (d, 2H), 7.63 (d, 2H), 7.21 (t, 2H), 6.94 (t, 2H), 6.06 (d, 2H), 4.06 (s, 3H), 1.75 (s, 18H). MALDI-TOF: m/z = 578.89 (calc. = 578.24).

#### BDP2

(4-methoxycarbonyl)arylbis(3-formyl-4,7-dihydro-2H-isoindolyl)methane
(10) 54 mg (8.55x10<sup>-5</sup> mol, 1 eq) of 9 were dissolved in 3 mL of TFA under Ar

 $<sup>^{\</sup>rm IX}{\rm The}$  color may vary from metal green to purple depending on the precipitation/evaporation conditions



at RT, left to stir for 5 min, than cooled to 0 °C and left to stir for 30 min. 0.1 mL (9.14x10<sup>-5</sup> mol, 10.7 eq) of trimethyl orthoformate were added dropwise and the reaction was allowed to warm to RT. After 30 min the solution was poured into ice/H<sub>2</sub>O, extracted with DCM, washed 3 times with aqueous Na<sub>2</sub>CO<sub>3</sub> 10%, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The crude was purified with SiO<sub>2</sub> column<sup>X</sup> (DCM/THF 1:1) to yield 21 mg (4.77x10<sup>-5</sup> mol, 52%) of product as a brownish solid.

(4-methoxycarbonyl)arylbis(3-formyl-isoindolyl)methene (BDP2) 16.1 mg ( $3.66 \times 10^{-5}$  mol, 1 eq) of 10 were dissolved in 5 mL of THF at RT, than 41.5 mg ( $1.83 \times 10^{-4}$  mol, 5 eq) of DDQ were added (the solution darkens in a few minutes) and the reaction was refluxed for 4 h<sup>XI</sup>. The solution was then diluted with DCM, washed 4 times with aqueous Na<sub>2</sub>SO<sub>3</sub> 10%, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated. The crude was purified by SiO<sub>2</sub> chromatography (DCM/THF 20:1) and precipitated 3 times from THF/hexane to give 13 mg ( $2.99 \times 10^{-5}$  mol, 82%) of product as a bronze-like solid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>:  $\delta = 10.38$  (s, 2H), 8.38 (d, 2H), 8.18 (d, 2H), 7.67 (d, 2H), 7.31 (t, 2H), 7.03 (t, 2H), 6.10 (d, 2H), 4.07 (s, 3H). MALDI-TOF: m/z = 434.79 (calc. = 434.13).

#### BDP3

(4-methoxycarbonyl)arylbis(3-carboxyl-isoindolyl)methene (11) 72.5 mg  $(1.25 \times 10^{-4} \text{ mol}, 1 \text{ eq})$  of **BDP1** were dissolved in 15 mL of TFA and left to stir at RT for  $6h^{XII}$ . The solvent was evaporated and the crude precipitated 3 times from THF/H<sub>2</sub>O,

<sup>&</sup>lt;sup>X</sup>The product might degrade on  $SiO_2$ , so column should be as fast as possible.

<sup>&</sup>lt;sup>XI</sup>The color of the solution changes towards a dark purple with presence of precipitate. The best way to follow the reaction is by UV-VIS absorption spectroscopy, using the same procedure used for purification to remove DDQ. Upon extraction the DCM phase will be deep blue and the precipitate disappears. The addition of a  $Zn^{2+}$  salt may be used to better distinguish the species in UV-VIS absorption spectroscopy.

<sup>&</sup>lt;sup>XII</sup>After 4h MALDI and UV-VIS absorption spectroscopy show completeness. To prepare sample for analysis evaporate several times with DCM to remove TFA. UV-VIS has to be done in DMF since in

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to yield 58 mg (1.25x10<sup>-4</sup> mol, 99%) of product as a purple solid. <sup>1</sup>H-NMR (400 MHz, DMSO- $d_6$ :  $\delta = 14.53$  (s, 1H), 13.66 (s, 2H), 8.31 (d, 2H), 8.11 (d, 2H), 7.81 (d, 2H), 7.27 (t, 2H), 7.05 (t, 2H), 5.99 (d, 2H), 3.98 (s, 3H). MALDI-TOF: m/z = 466.87 (calc. = 466.12).

(4-methoxycarbonyl)arylbis(3-dioctylcarbamoyl-isoindolyl)methene (BDP3) 9.7 mg (2.08x10<sup>-5</sup> mol, 1 eq) of 11 were dissolved in 15 mL of anhydrous DMA, then the solution was cooled to 0 °C. 30.1 mg (1.66x10<sup>-4</sup> mol, 8 eq) of CDMT and 46  $\mu$ L (4.16x10<sup>-4</sup> mol, 20 eq) of N-Me morpholine were added, followed by stirring at 0 °C for 2 h. 63  $\mu$ L (2.08x10<sup>-4</sup> mol, 10 eq) of dioctylamine were added at 0 °C<sup>XIII</sup> and the solution allowed to warm to RT and left to stir for 20 h. The solution was extracted with Et<sub>2</sub>O/H<sub>2</sub>O, washed 7-8 times with H<sub>2</sub>O, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated. The crude was then purified by SiO<sub>2</sub> chromatography (DCM/THF 100:1) to yield 3.13 mg (3.43x10<sup>-6</sup> mol, 16.5%) of product as a violet sticky oil. MALDI-TOF: m/z = 913.25 (calc. = 912.65).

## 3.3 Photophysical properties of BDPs

The photophysical properties of the three benzodipyrromethene (BDP) compounds were investigated in THF, which is known to be a good solvent for this class of molecules. In fact, their large planar aromatic structure can give rise to solubility issues, especially upon metal complexation, that induces a rigidification, strongly reducing the rotational mobility of the two isoindolic moieties.

The absorption spectra (Figure 3.5) show a non-structured, broad band in the visible

THF it aggregates.

<sup>&</sup>lt;sup>XIII</sup>Dioctylamine is insoluble in DMA and forms a white layer on the top of the solution, that slowly dissolves while the color of the solution changes from blue to violet. Addition as THF solution might be better.



Figure 3.5: Absorption spectra for compounds **BDP1** (red line), **BDP2** (green line) and **BDP3** (blue line) in THF.

region, which is responsible for the intense color of the molecules in solution. The band maxima and absorption coefficients are reported in *Table 3.3*.

Compound	BDP1	BDP2	BDP3
$\lambda_{ m max}/ m nm$ $arepsilon_{ m max}/ m cm^{-1}M^{-1}$	$\begin{array}{c} 565\\ 37400 \end{array}$	$582 \\ 36200$	$545 \\ 26600$

Table 3.1: Absorption properties of the three BDP ligands in THF

The position of the band maximum depends on the different  $\alpha$ -substituents, with the amide derivative (**BDP3**) being the most blueshifted. A progressive redshift is observed for the ester (**BDP1**) and formyl derivative (**BDP2**).

To gain a theoretical insight on the reasons of the spectral changes observed for the various substituents, we performed a series of DFT calculations, in which we followed a general three step procedure:

- Ground state optimization to find the minimum energy molecular structure.
- Vibrational frequencies calculation for ground state to verify that the minimum geometry is actually a real minimum. In fact, if the frequency value for a particular vibrational mode is imaginary, it means the optimization converged to a point in which that particular vibrational mode is in a maximum (i.e. we are in a saddle

point of the potential energy surface). Manually modifying the geometry along the vibrational coordinate allows the calculation to reach a real minimum.

• Vertical excitation energy at the ground state equilibrium geometry. This corresponds to the maximum of the experimental absorption band and it is the most widely used approach to predict experimental UV-VIS absorption spectra due to its low computational cost, since no calculation on the geometry of the excited state is needed (analytical solutions for the excited state Hessian are still not implemented in most computational software and numerical solutions are way more computationally costly).

The results are dependent upon the chosen basis set and functional. For the ground state optimization and vibrational frequencies calculation we used the B3LYP functional with 6-31+G(d,p) basis set, while for the vertical excitation (TDDFT) we used the PBE0 functional with 6-311+G(2d,p) basis set. For all calculations the solvent (THF) was taken in consideration through the PCM model.

To determine the basic structural features of BDPs and their influence on photophysics, we determined the ground state geometry and vertical excitation energy for compound **BDP1** with or without the presence of the meso aryl ring. *Figure 3.6* shows the HOMO and LUMO orbital shapes and energies for the two situations.



Figure 3.6: HOMO and LUMO orbital shapes and energies for **BDP1**, with (right) or without (left) the meso aryl ring.

The differences, both in energy and orbital shape, between the two situations are clearly negligible. This is due to the fact that the meso aryl ring is oriented
perpendicularly with respect to the plane formed by the benzodipyrromethene structure due to the steric hindrance of the isoindolic groups and thus conjugation is completely interrupted. This shows that it is possible to introduce any aryl substituent into the meso position without affecting considerably (actually the effect of vibrations at room temperature causes geometrical distortions that increase the amount of coupling) the photo- and electrochemical properties of the system, an interesting feature in view of future applications. Furthermore, it allows us to effectively model the structures with a reduced computational cost.

The orbital energies for the three compounds (*Figure 3.7(a)*) show a progressive decrease of both HOMO and LUMO energy in the order **BDP3** > **BDP1** > **BDP2**, but with a stronger effect on the LUMO, thus determining a progressive narrowing of the HOMO-LUMO gap. **BDP3** shows a substantial structural difference with respect to the other compounds (*Figure 3.7(b)*), showing an out-of-plane rotation of the carbonyl substituents due to the steric effect of the alkyl chains of the amide (modeled as -CH<sub>3</sub> to reduce the computational effort), so a reduction of conjugation should be considered as a factor contributing to the photophysical properties in addition to the electron withdrawing ability in the case of secondary amides.



Figure 3.7: (a) HOMO and LUMO orbital energy for the three BDPs (b) HOMO orbital shape on the optimized geometry for **BDP3**.

The low energy electronic transition calculated by TDDFT is almost completely dominated by the HOMO-LUMO transition for all the compounds, with no contribution from other excitations. The comparison between the experimental and calculated results is reported in *Table 3.3* and indicates a good agreement, showing the ability of the chosen computational approach to predict the effect of the substituents on the photophysical properties for this class of molecules.

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Compound	BDP1	BDP2	BDP3
$\lambda_{exp}/nm$	$565 \\ 550$	$582 \\ 569$	$545 \\ 524$
$\wedge_{calc}/$ IIII	550	509	524

Table 3.2: Experimental and calculated absorption maxima for the three BDP ligands in THF

#### 3.4 Photophysical properties of ZnBDP complexes

As described in the introduction, a pioneering study by Cheprakov and Vinogradov has shown the possibility to form luminescent  $\operatorname{Zn}^{2+}$  heteroleptic complexes upon reaction of either free-base benzodipyrrins or dimeric homoleptic complexes with  $\operatorname{Zn}(\operatorname{OAc})_2^{127}$ . However these species tend to evolve with time towards the formation of non-emissive homoleptic complexes.

Since our interest is focused on obtaining fluorescent heteroleptic complexes, we decided to use acetylacetonate (AcAc) as the ancillary ligand, exploiting the chelating effect of the two oxygens to improve the monomer stability<sup>133</sup>. Other types of ligands, such as bisoxazoline (BOX) have been proven to give stable heteroleptic complexes<sup>126</sup> and should outperform AcAc in this respect. However the introduction of the BOX ligand requires a further synthetic step or the addition of  $Zn(OAc)_2$  to a mixture of BDP and BOX, complicating considerably the system. Furthermore, the wide commercial availability of metal acetylacetonates allows for the possibility of testing different metals without the necessity to change the ancillary ligand, thus ruling out any possible unwanted effect on the photophysics.

The progressive addition of a  $6.98 \times 10^{-4}$  M ACN solution of  $\text{Zn}(\text{AcAc})_2$  to a  $2.25 \times 10^{-5}$  M solution of the ester **BDP1** was followed by UV-VIS absorption spectroscopy (*Figure* 3.8(a)). Upon  $\text{Zn}^{2+}$  complexation, a redshifted, very intense and vibrationally resolved band appears and the solution becomes strongly red-fluorescent. These absorption changes occurring upon addition of zinc (*Figure* 3.5) are typical of complexation by BDP, however the association constant could not be extracted easily due to the complex kinetics.

The same procedure used for **BDP1** was applied to **BDP2** and **BDP3**, to extract the spectral shapes of the corresponding heteroleptic complexes (*Figure 3.9(a)*). The emission shapes were recorded as well (*Figure 3.9(b)*), however the quantum yields and the excited state lifetimes are still under evaluation.

The photophysical properties of ZnBDP complexes are summarized in *Table 3.4*:

DFT calculation were performed analogously to what was done for the BDP ligands.

<sup>&</sup>lt;sup>133</sup>Guseva, G. et al. (2006). Russian Journal of Coordination Chemistry 32, 116–120.



Figure 3.8: (a) Spectrophotometric titration of a  $2.25 \times 10^{-5}$  M THF solution of **BDP1** with  $\text{Zn}(\text{AcAc})_2$  (6.98×10<sup>-4</sup> M in ACN) (b) Normalized absorbance variations at 626 nm with respect to the added equivalents of  $\text{Zn}^{2+}$ .

Compound	ZnBDP1	ZnBDP2	ZnBDP3
$\lambda_{ extbf{max,abs}}/ extbf{nm}$	626	660	588
$arepsilon_{ m max}/ m cm^{-1}M^{-1}$	88000	80500	71500
$\lambda_{ extbf{max,em}}/ extbf{nm}$	644	674	610

Table 3.3: Absorption and emission properties of the three ZnBDP complexes in THF

By directly comparing the orbital shapes and energies (*Figure 3.10(a)*) between **BDP1** and its zinc complex, one notices a symmetrization in shape and a small variation in energy, with both HOMO and LUMO slightly shifted towards higher energies, but with a stronger effect on the HOMO, leading to a decrease of the HOMO-LUMO gap. Although the modeling still qualitatively predicts correctly the relative order in the HOMO-LUMO gap (*Figure 3.10(b)*), this time the agreement between experimental and calculated values is less good (*Table 3.4*), suggesting that the functional performs better for free-base benzodipyrrin ligands than for their zinc complexes.

Further studies are undergoing to test different functionals, but a different and equally accurate strategy to predict the behaviour of new derivatives might be to model the ligands and then add an empirical energy difference based on the spectroscopic evidences obtained for the three investigated compounds. Chapter 3. Benzodipyrrins and their metal complexes: exploring new roads in fluorescence



Figure 3.9: Absorption (a) and fluorescence (b) spectra of the three complexes **ZnBDP1** (red line,  $\lambda_{ex} = 525$  nm), **ZnBDP2** (green line,  $\lambda_{ex} = 360$  nm) and **ZnBDP3** (blue line,  $\lambda_{ex} = 525$  nm) in THF.

Compound	BDP1	BDP2	BDP3
$\lambda_{ extbf{exp}}/ extbf{nm}\ \lambda_{ extbf{calc}}/ extbf{nm}$	$626 \\ 564$	$660 \\ 585$	$588 \\ 523$

Table 3.4: Experimental and calculated absorption maxima for the three ZnBDP complexes in THF

#### 3.5 Unexpected reactivity of ZnBDP2

Although the ester **ZnBDP1** and the amide **ZnBDP3** are stable in dilute THF solutions  $(10^{-5}-10^{-6} \text{ M})$  for days, showing only minor conversion to the homoleptic complex, this is not the case for the formyl derivative **ZnBDP2**. For this compound, an unexpected reaction occurs in minutes in the cuvette, with progressive disappeareance of the red emission and a simultaneous rise of a green one.

The reaction was followed by UV-VIS absorption spectroscopy after addition of 2 equivalents of  $Zn(AcAc)_2$  (1.53x10<sup>-3</sup> M in ACN) to a 1.39x10<sup>-5</sup> M THF solution of **BDP2**. The spectral changes are shown in *Figure 3.11(a)*, with the appeareance of a structured band around 500 nm, which was found responsible for the observed green emission through excitation spectroscopy. The absorbance changes at 660 nm (*Figure 3.11(b)*), directly proportional to the decrease in concentration of **ZnBDP2** through Lambert-Beer law, are compatible with a complex kinetics behaviour. In particular, what it seems to be an induction period in the first minutes, is actually a superposition of two processes: the **ZnBDP2** formation kinetics, that leads to an increase in absorbance



Figure 3.10: (a) HOMO and LUMO orbital energy for the **BDP1** and **ZnBDP1** (b) HOMO and LUMO orbital energy for the three ZnBDPs.

(as clearly visible from the very first spectra and data points, indicated by the arrows in *Figure 3.11*), and the unknown reaction, responsible for its decrease. On a longer time scale the reaction shows two different regimes, a first, fast one followed by a slower one. This type of behaviour indicates a multi-step mechanism, in which the rate-limiting step is not the same for all the course of the reaction.

To understand if the unknown product is still a  $Zn^{2+}$  complex and if the reaction modifies the structure of the **BDP2** ligand itself, rather that being a structural modification due to a change in coordination geometry (e.g. with the formation of an octahedral rather than tetrahedral complex), we added solid 2,2'-dimethyl-bipyridine (Me<sub>2</sub>bpy) to the cuvette as a lignad for  $Zn^{2+}$ , in two different moments of the reaction. When Me<sub>2</sub>bpy was added immediately after complexation (*Figure 3.12(a)*), the initial spectrum of the **BDP2** ligand was completely recovered as expected (together with the appearance of a new band in the UV region due to the complexation of  $Zn^{2+}$  by Me<sub>2</sub>bpy), while when the addition was performed after 40 minutes from the Zn(AcAc)<sub>2</sub> addition (*Figure 3.12(b)*), the initial ligand was reformed only partially, corresponding to the unreacted **ZnBDP2** fraction. Moreover, the structured absorption around 500 nm was converted in a broad gaussian-like band at about 440 nm. This behaviour indicates that the green emissive species is actually a zinc complex, with the reaction occurring on the **BDP2** ligand and leading to a significant blueshift in the absorption spectrum, compatible with a decrease in the conjugated path.

Trying to investigate the effect of the **BDP2** and  $Zn(AcAc)_2$  concentrations on the reaction rates, confusing results were obtained, but this effort permitted us to make two experimental observations:

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Figure 3.11: (a) Absorption spectra of a  $1.39 \times 10^{-5}$  M solution of **BDP2** + 2 eq  $Zn(AcAc)_2$  in THF at different time intervals (from red to blue). (b) The normalized value of absorbance at 660 nm versus time, used to monitor **ZnBDP2** concentration.

- Light speeds up the reaction: the reaction was followed by taking UV-VIS absorption spectra at fixed time intervals, using the same range, scan speed and instrument. It was observed that passing from the usually employed routine, that involves taking about 40 scans in the first 2 hours, to a "dark" routine composed of only 4 scans, leads to a significant decrease in the reaction rate. It is important to note anyway that the extent of the reaction is not compatible with the fact that the reaction "needs" light to occur, but it clearly proceeds even in the dark, although not as fast.
- The solvent used to prepare the Zn salt solution affects the reaction rate: even though the  $Zn(AcAc)_2$  solution in ACN was concentrated enough to allow the use of small volumes (~10<sup>-5</sup> L in 2x10<sup>-3</sup> L of the THF solution of **BDP2**), the presence of a polar, coordinating solvent appears to be detrimental for the reaction, as assessed by using different concentrations (and consequently different addition volumes) of  $Zn(AcAc)_2$  in ACN and by switching the solvent from ACN to acetone, which lead to an higher reaction rate.

Taking these two points in consideration, we decided to use always the same routine and instrumentation, to be sure to have always the same quantity of light hitting the cuvette, and we changed the zinc counteranion from acetylacetonate to tert-butyl acetylacetonate, here named TMHD after its IUPAC name (TMHD = 2,2,6,6-tetramethyl-3,5-heptanedionate). The presence of the two tert-butyl groups strongly increases the solubility in organic solvents, allowing us to prepare THF solutions that were concentrated enough to be used in our experiments, thus performing the



Figure 3.12: (a) Absorption spectra of **BDP2** (red), immediately after addition of 5 equivalents of  $Zn(AcAc)_2$  (green) and after addition of solid Me<sub>2</sub>bpy (blue). (b) Absorption spectra of **BDP2** (red), 40 minutes after addition of equivalents of  $Zn(AcAc)_2$  (green) and after addition of solid Me<sub>2</sub>bpy (blue).

measurements in pure THF and eliminating any effect from other solvents.

#### 3.6 Kinetics of ZnBDP2 reaction

With these preliminary observations in mind, we investigated the reaction kinetics in THF, upon addition of  $Zn(TMHD)_2$  (THF solution), to understand the role of the species concentration and of temperature. First, we recorded the spectral changes upon addition of 2 equivalents of  $Zn(TMHD)_2$  to a  $2.83x10^{-5}$  M solution of **BDP2** in THF, over a longer time range than ever before (*Figure 3.13(a)*). This allowed us to observe a second process, corresponding to the disappearence of the green emissive complex (**ZnG**) and contemporary rise of a blue emissive species.

The kinetic traces (Figure 3.13(b)) are too complex to be modeled without further details on the reaction mechanisms, and any attempt to figure out a reaction order for any of the involved species failed. However it was possible to understand that the second reaction appears slower than the first one, leading to a fast rise of the **ZnG** concentration, which remains around its maximum level for a sufficient interval of time to induce to think that a preparative isolation of the species may be possible.

The kinetic traces recorded upon variation of the amount of  $Zn(TMHD)_2$  (1, 2 and 4 equivalents) are shown in *Figure 3.14(a)*. If a clear increase in both reaction rate and amount of conversion was observed passing from 1 to 2 equivalents, no further improvement appears for 4 equivalents and actually the best reaction conditions appear

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Figure 3.13: (a) Absorption spectra of a  $2.83 \times 10^{-5}$  M solution of **BDP2** + 2 eq  $\text{Zn}(\text{TMHD})_2$  in THF at different time intervals (from red to blue). (b) The value of absorbance at 630 nm (**ZnBDP2**, blue), 485 nm (**ZnG**, green) and 390 nm (mainly blue species, red) versus time.

to be when a 1:2 ratio between the species is applied. Another strange behaviour was observed after a tenfold increase of the **BDP2** concentration (*Figure 3.14(b)*), with the reaction proceedingly with a rate very similar to the more diluted case, but with a lower amount of fractional conversion at any fixed time. Only with respect to temperature (*Figure 3.14(c)*), the reaction rate behaves as expected, with higher temperature favouring the reaction.



Figure 3.14: Absorbance at 630 nm (**ZnBDP2**) verus time in different conditions: (a)  $[BDP2] = 2.83 \times 10^{-5}$  M with 1 (blue), 2 (red) or 4 (green) equivalents of  $Zn(TMHD)_2$  added (T = 20 °C); (b) Addition of 2 equivalents of  $Zn(TMHD)_2$  to a 2.83x10<sup>-5</sup> M (red) or 2.83x10<sup>-4</sup> M (blue) solution of **BDP2** (T = 20 °C); (c) Addition of 2 equivalents of  $Zn(TMHD)_2$  to a 2.83x10<sup>-5</sup> M solution of **BDP2** at 20 °C (red) and 40 °C (blue).

Even though no explaination can be produced to rationalize the observed effects, what appears clear is that a preparative workup can be designed, taking into consideration the fact that the solution should be kept as diluted as possible and that an increase in temperature should promote the reaction without giving rise to unwanted side reactions.

#### 3.7 Synthetic preparation of ZnG

Taking into consideration what was learned from the photophysical measurements, a synthetic procedure was attempted on a small quantity of **BDP2**, to try to isolate the **ZnG** complex.

In a 250 ml round bottom flask, 20 mg ( $4.6 \times 10^{-4}$  M) of **BDP2** were dissolved in 100 mL of THF, than 50 mg of  $Zn(TMHD)_2$  (~ 2.5 equivalents) were added and the solution was left to stir at RT.

Surprisingly, nothing happened. Curiously, it was noticed that upon 1:10 dilution of the mixture in THF, a strikingly different behaviour was observed depending on the type of THF used:

- *THF for synthesis*: the reaction didn't proceed at all.
- THF for spectroscopy (Uvasol): the reaction was completed in about 2 hours.

Suspecting a role of the stabilizers contained in the THF for synthesis (i.e. BHT = dibutylhydroxytoluene, used to avoid the formation of peroxides), the solvent was evaporated and replaced with 100 mL of distilled THF. After O/N the reaction was found to be nearly completed by UV-VIS absorption spectroscopy. The solvent was evaporated and purification was attempted by SiO<sub>2</sub> column chromatography (DCM/THF 8:2). Unfortunately, due to the strong tendency of the product to aggregate, it got stuck in the column and it was practically impossible to recover.

At this point, a kinetic measurement was repeated in presence of 10 equivalents of BHT with respect to **BDP2** in spectroscopic THF. Surprisingly, the reaction worked as usually.

Learning from the previous failure, we redesigned the synthesis in order to try to isolate not the **ZnG** complex, but only its ligand, trying to remove zinc before running the chromatography to improve solubility:

In a dried 100 mL round bottom flask, kept under N<sub>2</sub> atmosphere, 10 mg of **BDP2** were dissolved in 50 mL of distilled THF ( $4.6 \times 10^{-4}$  M) and left to stir at RT for 3 h. The reaction was found to proceed very slowly, so the reaction was put to reflux and after 3 h was found to be completed by UV-VIS absorption spectroscopy. The solvent was evaporated and redissolved in DCM, then washed 3 times with acidic water (HCl(37%)/H<sub>2</sub>0 1:75), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated. The product was

then purified by  $SiO_2$  column chromatography (DCM/THF 8:2) to obtain 7 mg of nearly pure product. To further purify it for the spectroscopic and MS measurements, a part of it was precipitated from DCM/hexane and collected by centrifugation (3 cycles).

To check if the obtained product was really the ligand of **ZnG** complex, it was dissolved in THF and  $\text{Zn}(\text{TMHD})_2$  was added progressively, restoring the absorption shape observed in the kinetics (*Figure 3.15(a)*). The solution became brightly green emissive, and the emission spectrum is reported in *Figure 3.15(b*).



Figure 3.15: (a) Absorption spectra of a  $4.43 \times 10^{-5}$  M solution of the isolated ligand upon progressive addition of  $\text{Zn}(\text{TMHD})_2$  in THF (from red to blue). (b) Emission spectrum of ZnG in air equilibrated THF ( $\lambda_{exc} = 450$  nm).

An LC/MS measurements gave a result of m/z = 423, compatible with the loss of a -CH<sub>2</sub> group from **BDP2** (MW = 434.44). More complicate ad intriguing is the <sup>1</sup>H-NMR spectrum:

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta = 9.92$  (s, 1 H), 8.18 (d, 2 H), 8.03 (br. s, 1 H), 7.88 (d, 1 H), 7.87 (br. s, 1 H), 7.55 (d, 2 H), 7.49 (t, 1 H), 7.46 (d, 1 H), 7.44 (t, 1 H), 7.33 (t, 1 H), 6.76 (d, 1 H), 4.00 (s, 3H). Two protons (a doublet and a triplet) are missing, but observing the shape of the CDCl<sub>3</sub> peak near its base, it is probable that they lay under it.

Before discussing it, a few points should be taken in consideration:

• *Effects of concentration*: Progressively increasing concentrations were prepared and measured, to try to find the best possible conditions to run 2D routines, that can provide useful informations but normally require higher concentration to have a good signal to noise ratio. During this process it was noticed an aggregation process, that didn't allow us to collect good 2D spectra, but was very useful to separate the peaks of our product from those of impurities (the only ones that weren't changing).

• 2D and <sup>13</sup>C spectra: Although they gave only partial informations (due to longer acquisition times required) or were affected by aggregation, <sup>13</sup>C, COSY, NOESY and TOCSY were measured. The little that could be assessed was in agreement with what we state in our discussion on <sup>1</sup>H-NMR, in particular regarding the asymmetry of the conjugated structure, however we won't discuss them here.



Figure 3.16: <sup>1</sup>H-NMR spectrum of **BDP1** (above) and the synthesized ligand (below) in  $CDCl_3$  (downfield region). The singlet at 6.98 ppm belong to an impurity.

In *Figure 3.16* is shown the downfield part of the <sup>1</sup>H-NMR spectrum recorded for the isolated ligand. All peaks of the compound fall into this region, except for the methylic hydrogens of the methyl ester on the meso ring, whose signal is a singlet at 4.00 ppm whose integral was conveniently fixed to 3. The peak at 6.98 ppm is an impurity, the one at 7.26 is CHCl<sub>3</sub>, all other peaks belong to the isolated compound. The spectrum shows:

- *Two doublets at 7.55 and 8.18 ppm*: Both signals integrate for 2 protons and are assigned to the 4 protons on the meso ring.
- A double series of doublets and triplets at 6.76, 7.33, 7.44, 7.46, 7.49, 7.88 ppm: Each signal integrates for 1 proton. These signals can be attributed to the

isoindolic rings and the fact that two series are observed indicates an asymmetry in the conjugated structure, that can be due only to a reaction on the  $\alpha$ -substituents.

- Two broad peaks at 7.87 and 8.03 ppm: Each signal integrates for 1 proton and they can be assigned to two N-H protons. This is interesting since in the starting material only one N-H proton was present.
- Only one CHO proton at 9.92 ppm: The signal integrates for 1, so that we can say that only one formyl group has survived. What is most intriguing in this case is the lack of any other proton belonging to the molecule in the entire spectrum. This is very particular since it is difficult to think to any transformation of the aldehyde into any other group not containing a C-H bond (protons linked to heteroatoms cannot in principle be excluded because sometimes they are not observed due to fast exchange with the solvent) and restricts a lot the number of possible transformations involved.

Even though all the data taken up to now cannot be used to state anything with absolute certainty and a synthesis has to be repeated on a larger scale to unambiguously characterize the obtained compound by NMR (<sup>1</sup>H and <sup>13</sup>C), MS and possibly single crystal X-Ray structure, an hypothesis can be made with a certain degree of accuracy.

#### 3.8 The Baeyer-Villiger hypothesis

Considering all the evidences obtained, and in particular the MS and <sup>1</sup>H-NMR measurements, which clearly show that the reaction occurs on one of the two formyl group with loss of a -CH<sub>2</sub> group and without any new C-H bond formed, we hypothesise that a Baeyer-Villiger oxydation may occur (scheme in *Figure 3.17(a)*), leading to the benzodipyrrinone compound shown in *Figure 3.17(b)*, and named **BDPN** from now on (benzodipyrrinone). Analogously, its  $Zn^{2+}$  complex (with TMHD as ancillary ligand) will be named **ZnBDPN**.

It should be noted that the ligand may exist in two tautomeric forms (*Figure* 3.17(b)), but NMR spectroscopy clearly shows a strong (if not total) predominance of the keto form (clearly noticeable by the presence of two N-H peaks). However the quality of the spectrum was not sufficient to distinguish the enol form in case it was present in small percentage.

In the case of **ZnBDPN**, we assumed the ligand participates in its enol form, since that would retain the monoanionic nature of the original ligand. However this is just an assumption and a characterization of the complex should be performed by <sup>1</sup>H-NMR to address this issue.



Figure 3.17: (a) Scheme of the Baeyer-Villiger oxidation and hydrolysis hypothesized mechanism (b) The isolated **BDPN** ligand.

In a Baeyer-Villiger reaction<sup>134</sup>, a peroxide or peroxyacid "inserts" an oxygen between the carbonylic and  $\alpha$  carbons of an aldehyde or ketone, leading to the formation of an ester which, in the specific case of aldehydes, is a formate ester. The formate ester is readily hydrolized in presence of water to release the corresponding alcohol and formic acid.

In our specific case however, apparently no peroxide or peroxyacid was present in the reaction mixture. However the precise reason for which BHT is added to THF as a stabilizer is to prevent the formation of peroxides upon exposure to UV light<sup>135</sup>, acting as a radical scavenger. Spectroscopic THF (Uvasol) doesn't contain BHT (that would absorb UV light, giving spurious signals in UV-VIS spectroscopy) and thus may contain peroxides. This explains both the dependence from light exposure and from the type of THF used. It should be noted that the hypothesis is consistent also with our experiment with BHT in spectroscopic THF since, if it is true that BHT may prevent the formation of "new" peroxides upon light exposure, it cannot stop the Baeyer-Villiger reaction due to previously formed ones, since the mechanism is not radicalic.

Moreover, the observations made during the kinetics measurements can be rationalized:

- *The two-step mechanism* is consistent with the Baeyer-Villiger reaction followed by the formate ester hydrolysis.
- The unclear dependence from the reactants concentration since Zn(TMHD)<sub>2</sub> simply wasn't a reactant at all (although it cannot be excluded to have a role as catalyst through carbonyl activation) and the concentration of peroxide was unknown and affected by light irradiation. The inverse dependence of the fractional amount of product formed (after a fixed time) upon concentration is explained with the fact

<sup>&</sup>lt;sup>134</sup>Krow, G. R. (1993). Organic Reactions.

<sup>&</sup>lt;sup>135</sup>Klzilkilic, N. et al. (1980). Canadian Journal of Chemistry 58, 2819–2826.

that the peroxide was present as an impurity and of course the most the solution is diluted, the most of the compound can react before running out of peroxide.

To further test the hypothesis, we ran an experiment (*Figure 3.18*) in which **ZnBDP2** was formed in BHT stabilized THF, and the kinetics was followed for 15 minutes. Contrarily to what was observed with spectroscopic THF, only minimal changes were observed. At this point, 2 equivalents of mCPBA (m-chloro perbenzoic acid, 57-86% reagent grade), a well-known reagent for Baeyer-Villiger oxidations, was added. The reaction started immediately and proceeded fastly, then it nearly stopped. A second addition (same amount) restarted the reaction, clearly showing the role of mCPBA as a reagent and the validity of the hypothesis.



Figure 3.18: (a) Spectral changes in time after additions of mCPBA to a THF solution of **ZnBDP2** (b) The corresponding variation in time of absorbance at 660 nm.

Interestingly, after the second addition of mCPBA a spectral shape with a slightly blueshifted maximum with respect to **ZnBDP2** is observed. This spectrum was observed also during the kinetics experiments in the long times regime, however its intensity was very weak. It is possible that this spectral shape belongs to the orthoformate intermediate and it is better observed in this last experiment due to the different ratio of reaction rates between the Baeyer-Villiger and hydrolysis steps. A DFT calculation results in a vertical transition wavelength of 535 nm, qualitatively in accordance with the observed blueshift. Further experiments, such as addition of water to speed up the hydrolysis, are needed to adress this issue, that could be important to design a proper preparative strategy.

Assuming that a Baeyer-Villiger reaction is actually occurring, one can formulate a second hypothesis stating that the "green" to "blue" transformation may be actually



Figure 3.19: Scheme of the Baeyer-Villiger oxidation and hydrolysis hypothesized mechanism for the three emissive species.

the same reaction happening on the second formyl group, as shown in the scheme in *Figure 3.19*, but in absence of more accurate analysis we won't discuss it further.

#### 3.9 Conclusions

In conclusion, we have expanded the study of the photophysical properties of a new class of red-NIR luminescent molecules, metal benzodipyrrin complexes, towards the synthetic preparation of two novel derivatives, the formyl and amide, and compared their properties with an already published derivative, the ester, showing the validity of the approach in modulating the electronic properties of the species and thus their photo and electrochemical behaviour.

The comparison of the experimental data with theoretical calculations at the DFT level has allowed to gain a better insight on the influence of the  $\alpha$ -substituents and  $Zn^{2+}$  complexation on the energy of HOMO and LUMO orbitals, showing that the former influences preferentially the LUMO, while the latter has a bigger effect on the HOMO. The good predicting ability of the model can be effectively used to predict the properties of a derivative before attempting its synthesis, even though a more suitable functional has to be found for the zinc complexes.

Interestingly it has been observed in unpublished studies by the group of Vinogradov that benzodipyrrin ligands form luminescent complexes not only with zinc, but with a wide variety of metals (Ca<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Y<sup>3+</sup>, La<sup>3+</sup>, Gd<sup>3+</sup>, Yb<sup>3+</sup>). Both the type of metal and its counterion, acting as ancillary ligand, influence the spectral properties of the complexes, showing that a combination of these factors and the different  $\alpha$ -substituents can lead to a wide tunability in the red-NIR region.

A more detailed study should be performed to enhance the stability of the homoleptic complexes in polar solvents with the choice of an appropriate ancillary ligand and to evaluate the quantum yields and lifetimes of the complexes. Even though no quantitative study was performed yet, the compounds appeared stable upon light irradiation in time during our measurements, a crucial property for future applications.



Figure 3.20: Some possibilities offered by the rich chemistry of the formyl group to expand the class of benzodipyrrin metal complexes.

From a synthetic point of view, the preparation of the relatively reactive formyl derivative gives the possibility of a further expansion of the family of benzodipyrrin ligands thanks to its rich chemistry (*Figure 3.20*), enlarging the wavelength range and allowing the understanding of still unsolved questions, such as if the enhanced stability of the homoleptic complexes for benzodipyrrins with respect to dipyrrins is an effect of the expansion of the pyrrolic units or if it depends on the electron-withdrawing ability or steric hindrance of the  $\alpha$ -substituents used up to now.

A first and unexpected example of this rich reactivity has been observed in our studies in THF and attributed to a Baeyer-Villiger type reaction due to organic peroxides formed in solution upon light irradiation. A preliminar preparative attempt has shown the reproducibility of the process on synthetic scale and a further experiment has demonstrated that a classical reagent used in this type of chemistry, mCPBA, was very effective in promoting the reaction.

This type of chemistry, never applied to benzodipyrrins, cannot be included in the strategies to expand this family of ligands, since the obtained product belongs to a different class of compounds, that of dipyrrinones, that has unique and different properties.

Dipyrrinones are typically yellow chromophores, with an absorption band around 400 nm and an absorption coefficient of about 30000 cm<sup>-1</sup> M<sup>-1136</sup>. Upon excitation, they readily undergo by  $Z \rightarrow E$  isomerization and consequently they are essentially non-fluorescent<sup>137</sup>.

Extensive research by the group of Lightner has demonstrated that upon rigidification of the structure of xanthobilirubic acid, a naturally occurring dipyrrinone, through

<sup>&</sup>lt;sup>136</sup>Boiadjiev, S. E. et al. (2004). Journal of physical organic chemistry 17, 675–679.

<sup>&</sup>lt;sup>137</sup>Sakata, Y. et al. (2016). *Chemical Communications* 52, 1278–1281.

introduction of a carbonyl bridge between the two pyrrolic nitrogens, a brightly bluegreen emissive compound (named Xanthoglow by the authors) can be obtained<sup>138,139</sup>.



Figure 3.21: (a) The Xathoglow fluorophore discovered by Lightner (Reported with permission from ref. (138)). (b) The **ZnBDPN** complex shown as comparison.

Since this discovery, the same group has carried out a quite extensive research on the effect of substituents on the photophysical<sup>140</sup> and hydrogen-bonding<sup>141</sup> properties of this class of compounds.

Although they report an example of a dipyrrinone molecule in which one of the two pyrrolic units contains a benzofused ring (named "benzodipyrrinone" by the authors)<sup>142</sup>, a fully benzofused system has never been reported in literature to the best of our knowledge, and this would be the first example of a "dibenzodipyrrinone" ligand, a novelty that is analogous to the expansion of dipyrrins to benzodipyrrins.

Interestingly, to the best of our knowledge, this is the first example in which a metal ion has been used to induce the rigidification and generate fluorescence from dipyrrinones. Moreover, the presence of a formyl group on the  $\alpha$  position of the isoindolic moiety is ideal for the further synthetic modification of the structure and expansion of this completely new family of ligands and relative luminescent complexes.

<sup>&</sup>lt;sup>138</sup>Woydziak, Z. R. et al. (2005). The Journal of organic chemistry 70, 8417–8423.

<sup>&</sup>lt;sup>139</sup>Brower, J. O. et al. (2002). The Journal of organic chemistry 67, 2713–2716.

<sup>&</sup>lt;sup>140</sup>Boiadjiev, S. E. et al. (2004). Journal of heterocyclic chemistry 41, 1033–1037.

 $<sup>^{141}\</sup>mathrm{Ward},\,\mathrm{P.}$  et al. (2013). Supramolecular Chemistry 25, 286–291.

<sup>&</sup>lt;sup>142</sup>Boiadjiev, S. E. et al. (2003). Journal of heterocyclic chemistry 40, 181–185.

## Chapter 4

## Photoactive dendrimer for water photoreduction: a scaffold to combine sensitizers and catalysts

#### 4.1 Introduction

The quantity of energy that continuously arrives from the Sun far exceeds all human needs. It has been calculated that covering "0.16% of the land of the Earth with 10% efficient solar-conversion systems would provide 20 TW of power, nearly twice the world's consumption rate of fossil energy" <sup>143</sup>. Natural photosynthesis can accomplish this task directly by producing solar fuels, that is, converting the absorbed light into high-energy but kinetically stable chemical bonds.

Among various possibilities, water splitting into molecular hydrogen and oxygen represents one of the most promising, although very challenging, reaction schemes. Because water does not absorb visible light, a photosensitizer is needed. It has been reported in a seminal paper by Balzani et al.<sup>144</sup> that a simple chromophore like the well-known  $[Ru(bpy)_3]^{2+}$  complex can be used as a photosensitizer to drive the water photolysis in the presence of suitable catalysts. Since then, much effort has been

<sup>&</sup>lt;sup>143</sup>Balzani, V. et al., Energy for a sustainable world: from the oil age to a sun-powered future, 2010.
<sup>144</sup>Balzani, V. et al. (1975). Science 189, 852–856.

devoted to the construction of molecular systems for  $\mathrm{oxygen}^{145,146}$  and hydrogen  $^{78,147-156}$  generation.

Platinum (Pt) has a low overpotential for hydrogen evolution<sup>157</sup>. Because it is costly and resource-limited, a number of approaches based on Pt nanoparticles have been pursued to maximize the catalytic efficiency on a per atom basis<sup>158–160</sup>. Different scaffolds have been proposed for the synthesis of the nanoparticles, but one of the most promising is constituted by dendrimers.

Dendrimers<sup>161-164</sup> are repeatedly branched tree-like macro-molecules that exhibit a defined structure and a high degree of order in a restricted space. By using suitable synthetic strategies, selected functional units can be placed in predetermined sites of their structure. Dendrimers can also perform as nanocontainers and templates for the synthesis of metal nanoparticles. In their internal dynamic cavities, they can host metal ions, which can be reduced to form nanoparticles under suitable experimental conditions. Therefore, dendrimers have a two-fold task: at first, ligand for metal ions, then, templates and stabilizers to prevent nanoparticle aggregation. In the present approach, we couple these two functions to a third one: the photosensitization for the reduction of water to hydrogen, performed by the chromophores present at the dendrimer periphery.

The investigated system is constituted by a fourth-generation polyamidoamine (PAPAM) dendrimer with 32  $[Ru(bpy)_3]^{2+} \cdot 2$  Cl<sup>-</sup> metal complexes at the periphery<sup>165,166</sup> (*Figure 4.1*, hereafter referred to as RuPAMAM). We report on the synthesis of platinum

<sup>&</sup>lt;sup>145</sup>Cady, C. W. et al. (2008). Coordination chemistry reviews 252, 444–455.

<sup>&</sup>lt;sup>146</sup>Sartorel, A. et al. (2013). Chemical Society Reviews 42, 2262–2280.

<sup>&</sup>lt;sup>147</sup>Fihri, A. et al. (2008). Angewandte Chemie 120, 574–577.

<sup>&</sup>lt;sup>148</sup>Dempsey, J. L. et al. (2009). Accounts of chemical research 42, 1995–2004.

<sup>&</sup>lt;sup>149</sup>McCormick, T. M. et al. (2010). Journal of the American Chemical Society 132, 15480–15483.

<sup>&</sup>lt;sup>150</sup>Natali, M. et al. (2013). Chemistry-A European Journal 19, 9261–9271.

 <sup>&</sup>lt;sup>151</sup>McNamara, W. R. et al. (2012). Proceedings of the National Academy of Sciences 109, 15594–15599.
 <sup>152</sup>Sun, Y. et al. (2013). Chemical Science 4, 118–124.

<sup>&</sup>lt;sup>153</sup>Natali, M. et al. (2014). Chemical Communications 50, 1842–1844.

 $<sup>^{154}</sup>$ Luo, S.-P. et al. (2013). Angewandte Chemie 125, 437–441.

<sup>&</sup>lt;sup>155</sup>Helm, M. L. et al. (2011). *Science 333*, 863–866.

<sup>&</sup>lt;sup>156</sup>Han, Z. et al. (2012). Angewandte Chemie International Edition 51, 1667–1670.

<sup>&</sup>lt;sup>157</sup>Markovic, N. et al. (1997). The Journal of Physical Chemistry B 101, 5405–5413.

<sup>&</sup>lt;sup>158</sup>Takahashi, M. et al. (2013). Angewandte Chemie International Edition 52, 7419–7421.

<sup>&</sup>lt;sup>159</sup>Esposito, D. V. et al. (2010). Angewandte Chemie International Edition 49, 9859–9862.

<sup>&</sup>lt;sup>160</sup>Harriman, A. (1990). J. Chem. Soc., Chem. Commun. 1, 24–26.

<sup>&</sup>lt;sup>161</sup>Campagna, S. et al., Designing dendrimers, 2011.

<sup>&</sup>lt;sup>162</sup>Tomalia, D. A. et al., Dendrimers, dendrons, and dendritic polymers: discovery, applications, and the future, 2012.

<sup>&</sup>lt;sup>163</sup>Caminade, A.-M. et al., Dendrimers: towards catalytic, material and biomedical uses, 2011.

<sup>&</sup>lt;sup>164</sup>Astruc, D. (2012). Nature chemistry 4, 255–267.

<sup>&</sup>lt;sup>165</sup>Storrier, G. D. et al. (1999). *Langmuir* 15, 872–884.

<sup>&</sup>lt;sup>166</sup>Glazier, S. et al. (2002). The Journal of Physical Chemistry B 106, 9993–10003.



Figure 4.1: The 4<sup>th</sup> generation RuPAMAM dendrimer used in this study.

nanoparticles templated by the dendrimer scaffold and on the use of this system to produce molecular hydrogen by water reduction with the use of visible light and a sacrificial reagent. This is one of the few dendrimer-based systems reported in literature<sup>167,168</sup> for photocatalytic hydrogen production and the first one where both sensitizer and catalyst are anchored on a dendritic molecular scaffold.

### 4.2 Pt<sup>2+</sup> complexation by RuPAMAM dendrimers

The optical properties of the RuPAMAM dendrimer were analyzed using UV-Vis and fluorescence spectroscopy in H<sub>2</sub>O solution. The absorption spectrum of the dendrimer shows a ligand centered (LC) band at 288 nm and a metal-to-ligand charge-transfer (MLCT) band in the visible with a maximum at 455 nm (*Figure 4.2*). The emission band is slightly redshifted ( $\lambda_{max} = 618$  nm) with respect to that of the [Ru(bpy)<sub>3</sub>]<sup>2+</sup> complex in H<sub>2</sub>O ( $\lambda_{max} = 610$  nm) and the quantum yield is about the half (0.014).

The absoprtion and emission shapes are in accordance with what reported in literature for  $[Ru(Me_2bpy)(bpy)_2]^{2+}(169)$ , thus we attribute the small differences between RuPAMAM and the reference  $[Ru(bpy)_3]^{2+}$  to the presence of alkyl groups on one of the three bipyridine ligands in the dendrimer, together with the presence of amine groups that can quench the emission by electron transfer.

 $<sup>^{167}\</sup>mathrm{Yu},$  T. et al. (2012). The Journal of Physical Chemistry C 116, 10516–10521.

<sup>&</sup>lt;sup>168</sup>Yu, T. et al. (2013). Angewandte Chemie International Edition 52, 5631–5635.

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Figure 4.2: Absorption (black full line) and emission (green full line) of RuPAMAM in  $H_2O$  solution. For comparison, the absorption spectrum of  $[Ru(bpy)_3]^{2+}$  in the same solvent (red full line) has been reported.

In view of exploiting the well-known properties of the PAMAM skeleton as templates of metal nanoparticles<sup>61,170,171</sup>, we investigated the coordination of Pt<sup>2+</sup> metal ions by RuPAMAM. Upon titration of a RuPAMAM aqueous solution with K<sub>2</sub>PtCl<sub>4</sub>, small variations in the absorption spectra were observed: a decrease in the MLCT band and an increase in a tail below 500 nm (*Figure 4.3(a)*).



Figure 4.3: Absorption spectra (a) and emission spectra (b) of a  $1.47 \times 10^{-6}$  M solution of RuPAPAM in H<sub>2</sub>O upon titration with K<sub>2</sub>PtCl<sub>4</sub>. The inset shows the normalized emission intensity changes at 620 nm ( $\lambda_{ex} = 375$  nm).

More pronounced changes were observed in the emission spectra upon excitation at an isosbestic point (375 nm): the emission intensity decreases 80%. This quenching can be ascribed to the energy or electron-transfer processes between the <sup>3</sup>MLCT excited

<sup>&</sup>lt;sup>170</sup>Bronstein, L. M. et al. (2011). *Chemical reviews* 111, 5301–5344.

 $<sup>^{171}</sup>$ Yamamoto, D. et al. (2009). Langmuir 26, 2339–2345.

state of the ruthenium complex and the  $Pt^{2+}$  complex. The plot of the emission changes at 620 nm shows a plateau at ~20 equivs of  $Pt^{2+}$  per dendrimer (*Figure 4.3(b), inset*).

Several examples have been reported in which the metal complexation has been monitored by the absorption changes  $^{172-174}$ . To the best of our knowledge, this is the first example in which the stoichiometry of the Pt<sup>2+</sup> complex with a dendritic ligand can be evaluated directly from the emission spectra.

## 4.3 Reduction of $Pt^{2+}$ to PtNPs

After the complexation, the reduction of the platinum metal ions with sodium borohydride (NaBH<sub>4</sub>) has been performed. One equivalent (with respect to  $Pt^{2+}$ ) of NaBH<sub>4</sub> in water was added to a solution of RuPAPAM with 20 equivalents of  $Pt^{2+}$  per dendrimer to minimize the quantity of platinum ions outside the dendrimers. The solution was stirred for 24 h, and no precipitation was observed, confirming that almost all of the  $Pt^{2+}$  ions were stabilized by the dendrimers.



Figure 4.4: Absorption (a) and emission (b) spectra of RuPAMAM  $1.47 \times 10^{-6}$  M in H<sub>2</sub>O (black line), after addition of 20 eq. of K<sub>2</sub>PtCl<sub>4</sub> (red line) and after reduction with NaBH<sub>4</sub> (green line).

The absorption spectrum obtained after the reduction retained the typical features of the  $[\operatorname{Ru}(\operatorname{bpy})_3]^{2+}$  complex (*Figure 4.4(a)*) with the growth of a broad band all over the investigated spectral range, as typically observed for nanoparticle formation <sup>61</sup>. In addition, the emission intensity (*Figure 4.4(b)*) increased up to 50% of the initial value (emission before the addition of  $\operatorname{Pt}^{2+}$ ).

<sup>&</sup>lt;sup>172</sup>Yamamoto, K. et al. (2002). Nature 415, 509–511.

<sup>&</sup>lt;sup>173</sup>Yamamoto, K. et al. (2006). Bulletin of the Chemical Society of Japan 79, 511–526.

<sup>&</sup>lt;sup>174</sup>Imaoka, T. et al. (2013). Journal of the American Chemical Society 135, 13089–13095.

Because  $Pt^{2+}$  complexes are capable of quenching the ruthenium emission but the PtNPs do not act as quenchers<sup>175</sup>, from these emission data, we can estimate the number of  $Pt^{2+}$  ions reduced by the sodium borohydride. This estimate indicates that the borohydride added to the solution was capable of reducing ca. 40% of the  $Pt^{2+}$  ions coordinated by the dendrimers. Hereafter, to indicate the system RuPAMAM containing the platinum nanoparticles, the acronym RuPAMAM-PtNPs will be used.

To analyze the dimension, the structure, and the composition of the obtained nanoparticles, we have performed transmission electron microscopy (TEM) experiments.



Figure 4.5: (a) STEM image of RuPAMAM-PtNPs on holey carbon film copper grid. (b) Histograms showing the PtNPs size distribution. (c) HR-TEM image and fast Fourier transform (d) of a single nanoparticle.

*Figure 4.5a* reports a low-magnification STEM image, in which the contrast is proportional to the atomic number of the elements present. The Pt nanoparticles are clearly visible, represented by the bright white dots, while the dendrimers are represented by the lighter halo surrounding the nanoparticles.

Figure 4.5c shows a conventional high-resolution TEM image of a single nanoparticle, confirming at the same time the crystallinity of the nanoclusters and their composition: the interplanar distances of 0.19 and 0.22 nm (Figure 4.5d) correspond to the ones of crystalline Pt in the (1,0,1) direction. Moreover, the particle size distribution, obtained from the analysis of more than 200 particles, shows an average diameter of  $1.3\pm0.3$  nm (Figure 4.5b).

An estimate of the number of atoms per nanoparticle can be performed as follows. The average radius obtained from the HRTEM analysis is 0.65 nm and the volume

<sup>&</sup>lt;sup>175</sup>Brugger, P. A. et al. (1981). Journal of the American Chemical Society 103, 2923–2927.

is  $1.15 \times 10^{-21}$  cm<sup>3</sup>. Considering a density of the platinum of 21.45 g/cm<sup>3</sup>, a mass of  $2.47 \times 10^{-20}$  g can be obtained, and the number of moles is  $1.26 \times 10^{-22}$  mol. Multiplying the moles by the Avogadro's number, the average number of platinum atoms per nanoparticle results to be 76 Pt/NP. This result suggests that the particle formation involves at least the cooperation of three different dendrimers, not much for the dimension but for the average number of platinum atoms per nanoparticle. This is also confirmed by the EDX spectrum profile reported in *Figure 4.6*.



Figure 4.6: (a) STEM micrograph of a dendrimer aggregate including several platinum nanoparticles. (b) EDX profile taken along the yellow line reported in panel A. (c) EDX spectrum relative to the platinum nanoparticle highlighted with the red cross in panel a, corresponding to the first peak of Pt profile (black line) in panel B.

The Pt and Ru EDX profiles (*Figure 4.6b*) acquired along the yellow line highlighted in Figure 4a clearly show the increase in Pt and Ru signals inside the dendrimer as well as the Pt composition of the nanoparticles. This is confirmed by the EDX spectrum (*Figure 4.6c*) acquired on the nanoparticle marked with the red cross in *Figure 4.6a*. Chapter 4. Photoactive dendrimer for water photoreduction: a scaffold to combine sensitizers and catalysts

#### 4.4 Water splitting activity

Taking inspiration from the original paper by Balzani et al.<sup>144</sup>, the photocatalytic performance of the system was analyzed using ascorbic acid as a sacrificial electron donor. Hydrogen photoevolution was studied upon continuous irradiation with visible light of an argon-purged 1.6  $\mu$ M aqueous solutions of RuPAMAM-PtNPs at pH 5 in the presence of 0.1 M ascorbic acid and monitoring the gas phase of the reactor by GC. (For details, see the Supporting Information.)

The pH value of 5 was chosen on the basis of previous investigations<sup>154</sup> and for the following reasons: (i) lower pH values may lead to protonation of the PAMAM dendrimer thus determining release of the Pt nanoparticles from the core; (ii) too basic pH, on the contrary, increases the thermodynamic requirement for the hydrogen-evolving reaction, and (iii) pH 5 is high enough for almost complete deprotonation of ascorbic acid (pKa = 4.17 at 298 K) to favour reductive quenching of the ruthenium(II) sensitizer. As shown in *Figure 4.7(a)*, hydrogen evolution was observed.



Figure 4.7: (a) Photocatalytic hydrogen evolution obtained upon continuous visible light irradiation of a pH 5 water solution containing 1.6  $\mu$ M RuPAMAM-PtNPs and 0.1 M ascorbic acid (solid circles, solid line) and 34  $\mu$ M [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>, 2.1  $\mu$ M PAMAM-PtNPs and 0.1 M ascorbic acid (open circles, dashed line). (b) Comparison of absorption spectra before and after (5 h) irradiation of a pH 5 water solution containing 1.6  $\mu$ M RuPAMAM-PtNPs and 0.1 M ascorbic acid

Photocatalytic activity ceased after about 4 to 5 h of irradiation, achieving up to 95 nmol of hydrogen. According to the calculation previously reported, a 1.6  $\mu$ M RuPAMAM-PtNPs concentration corresponds to an average value of 1.51 nmol of Pt nanoparticles so that the turnover number (TON) is 63 per Pt nanoparticle. The maximum rate of hydrogen production, calculated in the linear part of the kinetic, is 67.2 nmol h<sup>-1</sup>, corresponding to a turnover frequency (TOF) of 44.5 h<sup>-1</sup> per Pt nanoparticle. Although different experimental conditions were used, comparison of the hydrogen evolving activity with supramolecular systems involving a ruthenium(II) polypyridine dye and a molecular catalyst shows that the present system displays TONs in line with those reported for Ru-Pd (TON = 56 after 29 h of irradiation)<sup>176</sup>, Ru-Rh (up to 60)<sup>177</sup> and Ru-Co (TON = 105 after 15 h)<sup>147</sup> dyads and considerably higher with respect to that for a related Ru-Pt one (TON = 4.8 after 10 h)<sup>178</sup>.

On the basis of previously reported homogeneous systems for hydrogen generation involving a ruthenium(II) trisbipyridine sensitizer and ascorbic acid sacrificial donor<sup>78,149,150</sup>, hydrogen production is likely to take place by first bimolecular reductive quenching of the sensitizer moieties by the ascorbic acid donor, followed by intramolecular electron transfer to the Pt nanoparticle catalyst. The confined Pt nanoparticles are indeed not capable of quenching the <sup>3</sup>MLCT excited state of the sensitizer (as observed by the recovery of the ruthenium-based emission after the reduction of the dendritic precursor with NaBH<sub>4</sub>), whereas ascorbic acid is known to quench reductively the excited state of  $[Ru(bpy)_3]^{2+}$  with a bimolecular rate constant of ca. 10<sup>7</sup> M<sup>-1</sup> s<sup>-1179</sup>.

The comparison of the absorption spectra before/after photolysis (*Figure 4.7(b)*) suggests that partial decomposition of the sensitizer occurs. This may be related to unproductive routes involving the photogenerated reduced form of the sensitizer and competing with electron transfer to the Pt nanoparticles<sup>78,149,150</sup>.

Control experiments in which the sensitizer was added externally as  $[Ru(bpy)_3]Cl_2 \cdot 6$ H<sub>2</sub>O salt (34  $\mu$ M to have the same sensitizer concentration of the previous experiment) to a water solution (pH 5) of PAMAM-PtNPs (2.1  $\mu$ M) in the presence of 0.1 M ascorbic acid showed a negligible amount of hydrogen produced. This evidence seems to suggest that an intimate contact between the sensitizer and the catalyst is required for efficient hydrogen generation. In particular, the dendrimer scaffold seems to act as a shield for the Pt nanoparticles, likely preventing or at least limiting bimolecular electron transfer to occur. Therefore, only when the ruthenium(II) sensitizer is directly connected to the catalytic site in the dendrimer supramolecule, electron transfer from the photo-generated reduced sensitizer can take place as an intramolecular process, thus contributing to hydrogen production.

<sup>&</sup>lt;sup>176</sup>Rau, S. et al. (2006). Angewandte Chemie International Edition 45, 6215–6218.

<sup>&</sup>lt;sup>177</sup>Elvington, M. et al. (2007). Journal of the American Chemical Society 129, 10644–10645.

<sup>&</sup>lt;sup>178</sup>Ozawa, H. et al. (2006). Journal of the American Chemical Society 128, 4926–4927.

<sup>&</sup>lt;sup>179</sup>Shan, B. et al. (2013). Inorganic chemistry 52, 4853–4859.

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#### 4.5 Conclusions

In conclusion, we have synthesized very small and monodisperse platinum nanoparticles in the interior of a dendrimer decorated by  $[\operatorname{Ru}(\operatorname{bpy})_3]^{2+}$  chromophores. The ruthenium complexes at the periphery of the dendrimer have the double role of "phosphorescent signaling units" to estimate the number of platinum ions hosted and photosensitizers in the light-induced water reduction process in the presence of a sacrificial electron donor. The system reported is the first example in which both sensitizer and catalyst are anchored on a dendritic molecular scaffold, as demonstrated also by HR-TEM analysis.



Figure 4.8: A graphical representation of the investigated system.

The present study provides a novel approach in the development of artificial photosynthesis based on intra- molecular processes by using photoactive dendrimers. The advantage of using photoactive dendrimers is the possibility to easily change the catalyst hosted in the supramolecular structure<sup>168</sup>, and, because of the versatility of the dendrimer chemistry, it is possible for synthesized molecules with a large variety of photoand redox- active moieties to achieve promising artificial photosynthetic systems.

# Chapter 5 Conclusions

In this thesis work, we have investigated the interaction between molecular species and nanoparticles to realize organic-inorganic architectures able to perform complex photophysical and photoelectrochemical functions.

In *Chapter 2*, we have coupled an organic D-A-D oligomer to SiNPs of two different sizes. We have demonstrated the ability of this system to act as a light harvesting antenna, considerably enhancing the ability of silicon nanoparticles to exploit visible light to generate its typical very long lived excited state. Even though direct experimental evidence was not produced (it will be the object of future investigations), the data are compatible with the possibility of electron transfer processes between the nanoparticle and the chromophore, a process that would be interesting for the integration of silicon nanoparticles in organic materials for optoelectronics. Moreover, the ability of the oligomer to act as an efficient two photon absorber has been exploited to realize one the first proof of principle cases of a two-photon antenna based on silicon nanoparticles (a similar example was reported for porous silicon particles<sup>180</sup>, a very similar material), a system that can be used to enhance the three-dimensional resolution, improve light penetration and reduce scattering effects in time-gated luminescence, in which porous silicon nanoparticles have been proven advantageous<sup>181,182</sup>. Even though our system was far from being optimal, it has allowed to elucidate the basic design principles for an efficient two-photon antenna based on silicon nanoparticles.

In *Chapter 3*, we have performed the synthesis of a family of red-NIR emissive zinc complexes of benzodipyrrins, a system that can be though as the extended version of the dipyrromethene scaffold used to form the brightly luminescent and very photostable BODIPY dyes. The final goal of the project is to couple these chromophores to silicon nanoparticles for a dual purpose: the study of energy transfer processes from the dye

<sup>&</sup>lt;sup>180</sup>Secret, E. et al. (2014). Advanced Materials 26, 7643-7648.

<sup>&</sup>lt;sup>181</sup>Gu, L. et al. (2013). Nature communications 4.

 $<sup>^{182}</sup>$  Joo, J. et al. (2015). ACS nano 9, 6233–6241.

to the nanoparticle (and possibly viceversa) and the fine control of nanoparticles aggregation, since these dyes are known to perform a kinetically controllable transformation from an homoleptic to an heteroleptic complex that can be followed spectroscopically thanks to a clear spectral signature arising from exciton coupling. Although the effective integration with nanoparticles was not not performed yet, the combined experimental and computational (DFT) analysis of the compounds has demonstrated the efficacy of the adopted strategy (modification of carbonyl groups in  $\alpha$  positions) in tuning the absorption and emission properties. Moreover, an interesting and unexpected process was observed for the case of formyl substituted benzodipyrrins, with the progressive disappearance of the red emission and growth of a bright green one upon a chemical transformation in solution, that from preliminary experiments (NMR, MS, effect of an appropriate reagent) was hypothesized to be due to a Baeyer-Villiger reaction involving peroxide species formed in the solvent (THF). The resulting benzodipyrrinone complex constitutes the first example of a new and totally unexplored class of luminescent species.

In Chapter 4, we have exploited a synthetic strategy to form platinum nanoparticles stabilized by dendrimers in water solution through the use of a photoactive dendrimer based on  $[Ru(bpy)_3]^{2+}$  complexes, with the aim of realizing a supramolecular system able to integrate all the required processes to perform the hydrogen evolving part of a full photosynthetic cycle, from light harvesting to catalysis. This complex and its integration with platinum are well known to photogenerate hydrogen in solution, but the reported systems up to now were based on diffusional processes, exploiting the long-lived excited state of the complex through the use of an electron relay that is able to transport electrons to the platinum catalyst. Although the efficiency of our system was not very high and suffered from the degradation of the photosensitizer, the demonstration of hydrogen generation constitutes an important proof of principle in the field, mainly for two reasons: the elimination of the necessity of an electron relay and the coupling of the catalyst and the photosensitizer in the same supramolecular assembly. This last feature is particularly interesting since it removes the requirement for long-lived excited states of the photosensitizers used in diffusion controlled processes, allowing the use of a vastly larger library of compounds, including for example the photochemically stable, highly absorbing and commercially available fluorescent species, exploiting the well developed chemistry of dendrimeric species.

In conclusion, this thesis work has further demonstrated the potential of nanomaterials and their hybrid systems in the field of photoinduced processes. While the main goal was to design systems for energy applications, occasional deviations from this aim were presented, like in the case of the two-photon antenna, a promising approach for bioimaging purposes (further showing the appeal of silicon nanoparticles for diverse research fields), or in the case of the serendipitous chemical transformation of formyl benzodipyrrins into benzodipyrrinones, leading to a completely new class of fluorescent species.

#### Chapter 5. Conclusions

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