Introduction

1. General perspective and motivation

Our society is facing tremendous challenges due to overpopulation, natural resource depletion and global warming, among many others. On the other hand, a fundamental part of our everyday lives relies on sophisticated technological applications. The combination of all these factors has naturally a direct impact on the needs that research must address.[1-4] In this sense, many efforts are being made by the scientific community to design advanced functional materials, which are already enhancing our life quality and satisfying our demands as a society. Particularly, in the field of optoelectronics, where light is controlled to fulfill our purposes in electronic devices, significant progress has been made in the last quarter of century.[5] Optoelectronics is an extremely interdisciplinary field, in which contributions from material scientists, chemists, physicists, and electronic engineers are crucial for the design and optimization of devices from a macroscopic viewpoint, as well as for the understanding of the physicochemical processes taking place at a molecular level.

The two prime examples of optoelectronic devices are solar cells and light-emitting diodes (LEDs). While the role of a solar cell is to convert light into electricity, the well-known photovoltaic effect, the opposite process takes place in LEDs: electricity is converted into electromagnetic radiation, a phenomenon known as electroluminescence. There are nowadays multiple photovoltaic (PV) technologies for solar energy conversion[6] as well as light-emitting diodes[7] based on different materials. Some of these technologies have been studied for a long time already, so they are well established and there is little room for improvement. However, there is still a significant amount of knowledge lacking on the fundamental processes taking place in more recent technologies, such as dye-sensitized solar cells (DSSCs)[8] or organic light emitting diodes (OLEDs).[9] The main difference between these two examples and traditional solar cells or LEDs is that in DSSCs and OLEDs, molecules are responsible for the absorption or emission of electromagnetic radiation, while in conventional technologies a semiconductor plays this role.

1.1 Photovoltaics

Solar cell technologies are usually categorized according to structural and or operative differences, in terms of generations.[10] Single junction silicon devices belong to the first

generation, while thin-film based designs are included in the second generation. The third generation embraces multijunction architectures together with emerging technologies. Because of the materials that compose the device and how it operates, each generation can achieve different efficiencies and the costs also vary (Figure 1). A recent comparison between mature and emerging PV technologies can be found in reference 11.
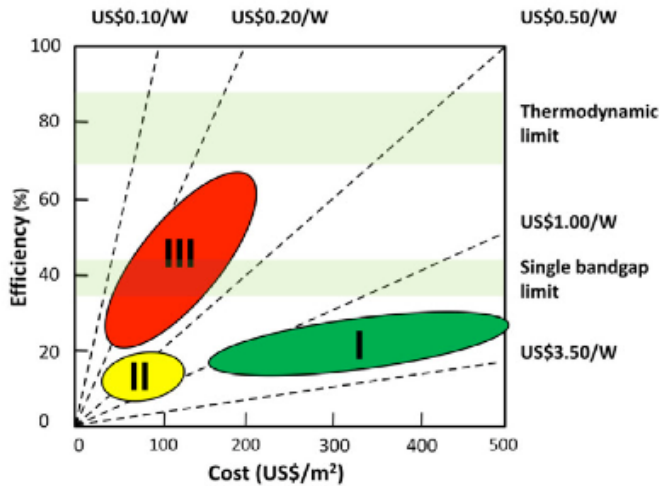

Figure 1. Efficiency and cost for first (I), second (II), and third (III) generation PV technologies. Taken from reference 12.

The first generation comprises traditional silicon-based solar cells and represented about 90% of the global PV production in 2015,[13] due to the compromise between cost and efficiency, as well as their high stability and longevity. The oldest and most popular first generation solar cells are those based on monocrystalline silicon, but their production cost is relatively high due to the controlled conditions needed for obtaining single crystals, for which a considerable amount of energy is required in their production. The production cost may be lowered by using polycrystalline silicon instead of single crystals, but this change is accompanied by a decrease in the solar cell efficiency. Second generation solar cells[14] were born to face the challenge of lowering the production costs while preserving the ~25% achieved efficiencies in first generation solar cells. They are based on thin-film technologies, where the semiconductor layer's thickness is of the order of nanometers to a few micrometers and are usually divided in three main subsets, depending on the semiconducting material responsible for light absorption: amorphous silicon, cadmium telluride (CdTe) and copper indium gallium selenide (CIGS).[15] The production costs of second generation solar cells are lower[10] than for first generation ones, since less semiconducting material is needed in thin-film technologies. However, their efficiencies

are also lower, of ~10-15%, compared to crystalline silicon based solar cells, mainly due to the presence of defects formed in the course of fabrication. On the other had, second generation devices are very suitable over crystalline silicon cells for several specific light conditions, such as diffuse light for instance.[16]

The major drawback in improving the efficiency of first and second generation solar cells is that they are based on a single p-n junction.[17] The efficiency of single junction devices is limited by thermodynamics to ~31%. This is known as the Shockley-Queisser limit,[18] and the purpose of third generation solar cells was to overcome this barrier. This may be achieved by combining multiple p-n junctions of different semiconducting materials in so-called tandem or multi-junction solar cells[19-21] allowing a broader range of the solar spectrum to be absorbed by combining semiconductors of different band-gaps. Efficiencies above 40% have been achieved[22] with such layouts (Figure 2), but the fabrication price is still too expensive due to the manufacturing complexity.
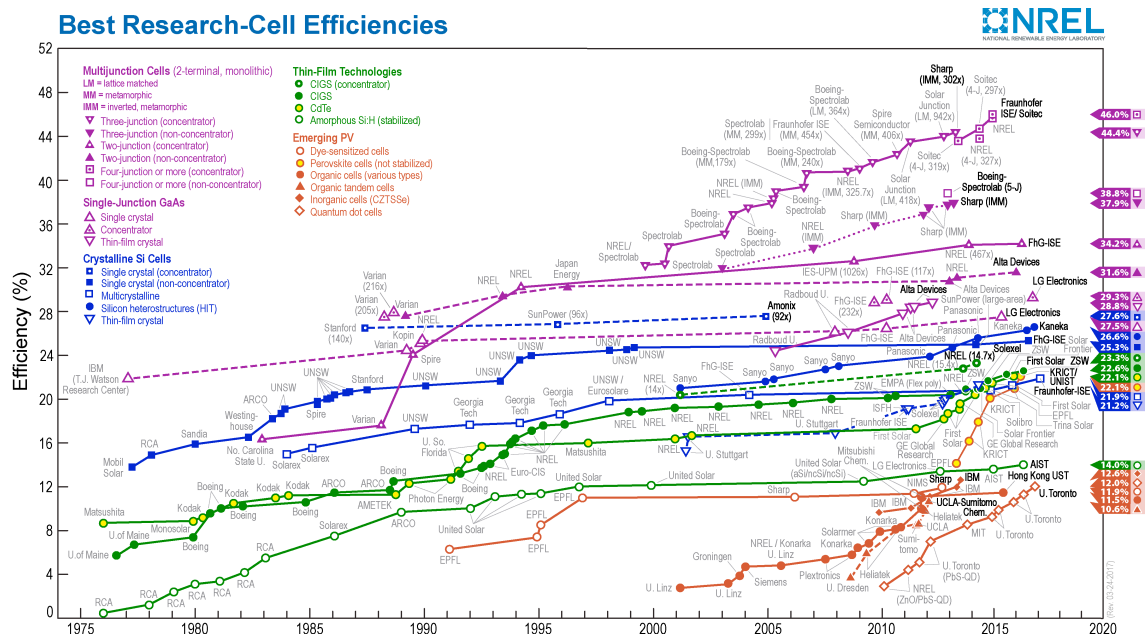

Figure 2. Plot of compiled values of highest confirmed conversion efficiencies for research cells, from 1976 to the present, for a range of PV technologies. Taken from reference 23.

Other emerging PV technologies are usually also classified as third generation due to their potential for large scale, low cost production, although to overcome the Shockley-Queisser limit efficiency, a tandem architecture of the device is needed. Examples of such emerging technologies include DSSCs,[24] organic solar cells,[25] or those based on quantum dots[26] or perovskites,[27] among others. They all possess several advantages in front of traditional

silicon solar cells, in particular, easier, cheaper, and scalable production along with versatile designs.[28] These technologies however are still far from being competitive in the PV market due to their, for now, limited efficiencies. Thus, intensive research on these emerging technologies is currently going on, from a fundamental point of view and to overcome difficulties of practical applications. In this sense, perovskite solar cells are a current example of how focused research may lead to an enormous improvement in their performance.[29] Perovskite solar cells have had the most rapid increase in power conversion efficiency in the history of solar cells, from 9.7% to 20.1% in only two years.[27]

1.1.1 Dye-sensitized solar cells

In 1991, professor Michael Grätzel and his coworker Brian C. O'Regan published a letter in Nature[30] reporting the fabrication of a "low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films", nowadays known as a DSSC or Grätzel solar cell. Although previous attempts were made to use dye-sensitized photoelectrochemical cells for solar energy conversion,[31-34] the problem was that the light-harvesting efficiencies of a monolayer of dye adsorbed on a smooth semiconductor surface were less than 1%.[30,35] The major breakthrough of Grätzel's and O'Regan's work was the use of a mesoporous semiconductor with high internal surface area, on which a monolayer of sensitizer was adsorbed. With this setup, a light-to-electric conversion efficiency of 7-8% was achieved, leading to a change in the paradigm of PVs. In 2010, Michael Grätzel was awarded the Millenium technology prize for his contributions to the field of DSSCs, because of its promising potential as a low-cost alternative to conventional silicon PVs.[36]

A very attractive characteristic of DSSCs is that the light harvesting and charge carrier transport tasks are separated, in contrast to standard silicon solar cells. In particular, dye molecules adsorbed on a mesoporous metal oxide semiconductor, usually TiO_2, are responsible for sunlight absorption. The operation principle of a DSSC[24] may be summarized as follows. After an incident photon is absorbed by the sensitizer, electron injection from an electronically excited state of the dye into the conduction band of the semiconductor takes place, leaving the dye oxidized. The circuit is closed by a counterelectrode that transfers the electron to a redox couple of an electrolyte and finally the sensitizer is regenerated back again by electron transfer from the reduced electrolyte to the oxidized sensitizer.

One of the principle features of DSSC with respect to other PV technologies is that every component of the cell carries out a different function. This allows to systematically study each process that takes place in the cell in an approximate independent manner. For instance, by testing different metal oxides, the electron injection and transport along the semiconductor may be optimized. By screening different materials, the light harvesting capabilities of the sensitizer can also be improved, as well as the electron transfer between the redox couple and the oxidized sensitizer. Another advantage is that DSSC panels can be easily manufactured by inexpensive roll-to-roll processing, converting them in a low-cost PV technology. In this regard, their fabrication is simple enough so that there are even kits available for hand-making your own DSSC using raspberry juice or flower extracts as the source of natural sensitizers.[37,38] In comparison to emerging pervoskite solar cells, in DSSCs the majority of components are non-toxic and abundant (except for Pt), although very little amounts of these expensive materials are actually needed. Another important characteristic is that they have a good performance in diverse light conditions, under diffuse light for instance, and at high temperatures.[24] As for their design, they can be flexible and thus attain non-conventional shapes, they are also thin, lightweight, transparent, and may appear in several colors making them specially attractive for architects and designers.[24] Due to the combination of all these desirable characteristics, several companies started to commercialize DSSC components and devices after the first investigations on this field and also many start-up companies appeared. Apart from rooftop panels, they are very promising for building-integrated PVs, that is for example, replacing typical materials from facades or conventional glass windows (Figure 3).[39] Many applications also point towards portable electronics, for powering small electronic devices, as well as for indoor or decorative purposes.[40]
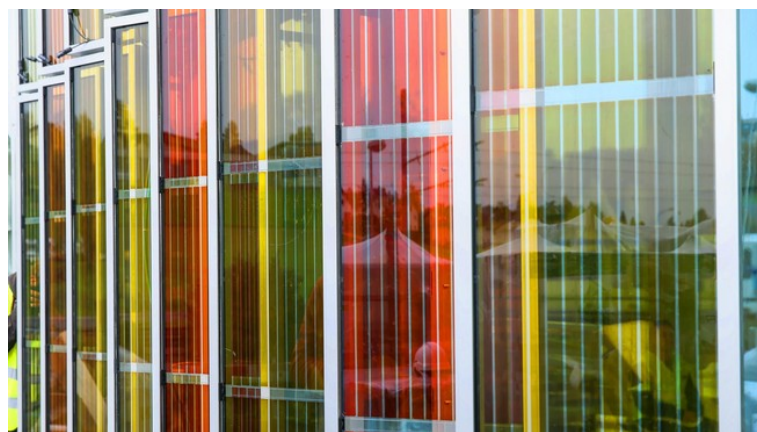

Figure 3. EPFL's (École Polytechnique Fédérale de Lausanne) convention center is equipped with a glass facade composed of DSSCs. Picture taken from reference 39.

Although the first years of research in DSSCs were very promising after the major advance of the 1991 Nature paper,[30] the evolution of the solar-to-electrical energy conversion efficiency of DSSCs did not improve as expected albeit all the research efforts and a sudden increase in the number of publications in the field.[24] In fact, validated efficiencies of module and submodule solar cells have increased rather slowly during the last twenty years, reaching a maximum of 12% in 2014 (Figure 2).[23] During these years, many research groups have claimed significant improvements of the efficiencies, but if these values are examined with perspective and a critical eye, one arrives to the conclusion that there has been no substantial improvement.[41]

A DSSC is based on three main components (Figure 4): a mesoporous oxide, a sensitizer and an electrolyte. Typically, a thin film of mesoporous TiO_2 (anatase) is deposited on a transparent glass plate coated with a thin layer of a transparent conducting oxide (TCO), usually fluorine-doped tin oxide (FTO), for charge transport out of the cell. Other several metal oxides such as ZnO or SnO_2 among others have also been tested, but TiO_2 gives the best performance.[42] A monolayer of sensitizer, responsible for the light harvesting process, is chemically anchored on the metal oxide nanoparticles. A plethora of sensitizers have been studied in recent years, ranging from organic dyes and porphyrins to organometallic complexes.[24] All these components constitute the photoanode of the DSSC. An organic solvent containing an electrolyte, with the iodide/triiodide (I^-/I_3^-) redox couple, is usually used to regenerate the sensitizer. The cathode coated with a thin catalytic layer of platinum catalyst deposited on a conducting glass substrate restores the redox couple and closes the circuit. The I^-/I_3^- redox system was the one used by Grätzel and O'Regan in their 1991 Nature paper,[30] and many other liquid electrolytes have been investigated since then.[43] However, liquid electrolytes have several practical problems: leakage, corrosion of the counterelectrode, and temperature stability issues.[24] As an alternative to liquid redox electrolytes, solid-state hole conductors have also been intensively investigated[43] in so-called solid-state DSSCs, but the efficiencies have not sensibly improved.[44]

The processes that take place in a typical DSSC based on TiO_2 and an I^-/I_3^- redox couple are simplified in the energy level diagram shown in Figure 5. When the sensitizer absorbs electromagnetic radiation it is promoted to an excited electronic state (step 0). From here, the molecule can decay back to its ground state, which would be a loss reaction (step 1), or the electron can be injected into the conduction band of the semiconductor (step 2). The

competition between these two processes is crucial for the performance of the device. The electron injection time scale is accepted to be in the femtosecond range,[24] while the lifetime of the molecular excited state is usually longer, thus fast electron transfer to the nanocrystalline TiO_2 takes place. The mesoporous metal oxide anode consists of a network of interconnected nanocrystals, where electron transport (step 4) takes place by diffusion after electron injection. This process however competes with recombination of electrons with the oxidized dye or the redox couple (steps 5 and 6 respectively). Those electrons that are collected at the anode then flow through the external circuit to the counterelectrode, where the oxidized redox mediator (I_3^-) is reduced to I^- ions (step 7). The circle is completed when the oxidized photosensitizer (S^+) is reduced by the I^- redox mediator (step 3), regenerating the photosensitizer (S) and I^- is oxidized back to the I_3^- species.
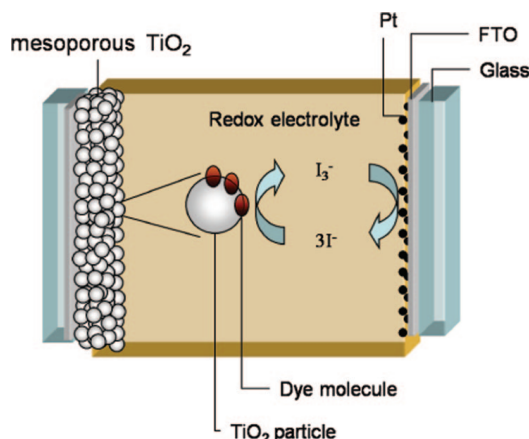

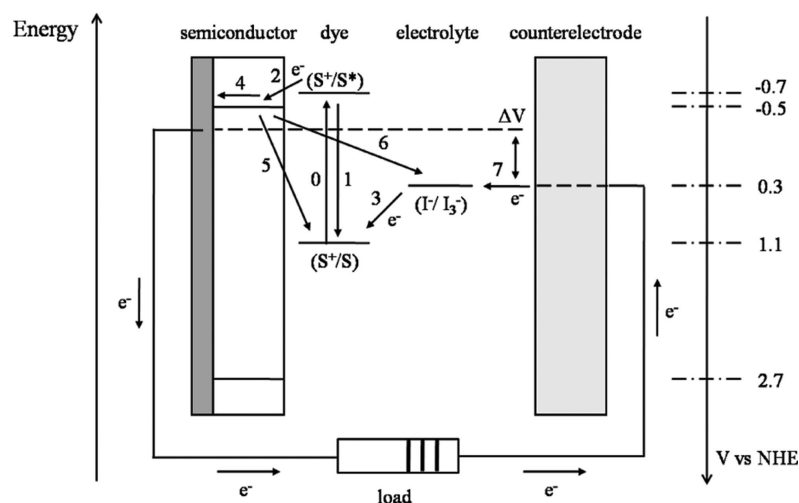**Figure 4.** Schematic representation of the main components in a typical DSSC. Taken from reference 24.

Figure 5. Schematic energy level diagram for a typical DSSC based on TiO_2 and the I^-/I_3^- redox couple. The main electron transfer processes are indicated by numbers (1-7). Taken from reference 24.

1.2 Lighting

The invention of the light bulb is probably one of the most important discoveries of the XIXth century due to its impact on the life of human beings. Nowadays, artificial light is everywhere and has become an essential commodity of our society. However, the elevated power consumption of traditional light bulbs together with related environmental issues has motivated the search of new lighting technologies.[45,46] The advances in nanotechnology produced over the last 40 years have lead to alternative light sources such as LEDs and OLEDs[47] with improved and desirable characteristics that are already having an impact in our everyday lives. New discoveries in the current century on advanced materials and physical phenomena related to the interaction of light with matter will certainly play a key role in the development of these new technologies, prompting economic and social changes worldwide.

1.2.1 Light-emitting diodes

Nowadays, the LED is the most rapidly-developing lighting technology and it is becoming increasingly present in our everyday life, mainly in screen panels, advertising illumination, traffic signals, television monitors, and automotive lamps among many others. This is due to their lower power consumption, longer lifetime, and greater energy efficiency compared to incandescent light bulbs. They also offer more design flexibility compared to conventional lighting technologies, making them appropriate for specialized medical equipment or for decorative purposes.

LED technology is based on a p-n junction, the interface between two doped semiconductors, one with excess of holes and the other with excess of electrons. When an appropriate voltage is applied, the depletion region (i.e. where charge carriers have been depleted) is narrowed, allowing charge carriers to cross the junction. This eventually leads to light emission when electrons and holes recombine, in a phenomenon known as electroluminescence. Different emission colors may be achieved by using semiconductors with different energy band gaps. For instance, the first usable LED[48,49] emitting in the visible region was developed by the General Electric Company back in the 1060's. Its semiconducting material was gallium arsenide phosphide (GaAsP) with red light emission. It wasn't until a decade later that other colors were developed, such as yellow or green, by wisely doping different inorganic semiconductors. Despite a wide range of LEDs emitting different colors was available at that time, their application as light sources was still

limited because they were not bright enough.[50] In the 1980's super-bright LEDs were developed and started to be cost efficient so that their commercial production began. The major progress in LED technology took place in the 1990's, when Akasaki, Amano and Nakamura succeeded in creating a bright blue LED, which had been a long-standing challenge due to practical difficulties.[51] They received the Nobel prize in physics in 2014 for their invention,[52] since this meant that white light could now be created with LED technology, thus becoming an alternative to incandescent and fluorescent lamps.[52] The key point in the LED illumination revolution is that, because lighting is responsible for about 20% of the global electricity consumption,[52] this new light source could have a great environmental and economic impact in a near future, since it is much more energy-efficient and longer-lasting than conventional light sources.

1.2.2 Organic light-emitting diodes

In 1987, researchers working at the Eastman Kodak company reported the first OLED, its novelty residing in the use of layers based on organic materials, in contrast to the traditional inorganic semiconductors used in LEDs.[53] They built a double layer device where diamine was used as the hole transporting layer while Alq3 ((tris(8-hydroxyquinoline)aluminum(III)) molecules operated as the electron transporting layer and emissive layer. In the diamine/Alq3 interface, electron-hole pairs bind to form excitons that deactivate radiatively by fluorescent emission. Two years later, the same researchers who developed the first practical OLED demonstrated that by doping the electron transporting material with different fluorescent dyes or by changing the dye concentration, the OLED emission color could easily be tuned.[54] Although the external quantum efficiency (the ratio of the number of emitted photons to the number of injected charge carriers) of these earliest OLEDs was quite low (< 3%), a lot of progress has been made to increase it in the past 20 years.[9] Moreover, the use of different materials, such as electroluminescent conductive[55] polymers or highly phosphorescent organometallic complexes,[56] has lead to a substantial improvement in the field, so that nowadays, the number of OLED displays hitting the market is continuously rising. In particular, several flat panel TVs, smartwatches, tablets, portable music players, digital cameras, and infinite models of smartphones are based on this technology. Although OLED TVs are still very expensive, they are "the best in the market" because of their improved and sharper image quality, as well as for their real deep black color compared to traditional liquid crystal display (LCD) screens. All these rapid advances suggest that in a near future the majority of smart devices

will be based on this technology. On top of that, due to the flexibility of OLED displays, it will become usual to have screens which can be bended, folded, or stretched. As for lighting applications, OLEDs are still deep behind LED technology, but further research will surely boost their use eventually. In fact, the same year Michael Grätzel was awarded the Millenium technology prize, Sir Richard Friend was also elected as one of the three laureates for his contributions in the field of OLEDs.[36]

A typical OLED architecture is shown in Figure 6, where layers of different materials performing different functions are sandwiched between two electrodes. On one extreme of the device there is a glass or plastic substrate and adjacent to it the anode, which is typically indium tin oxide (ITO). On the opposite extreme of the device there is a metal cathode, usually barium or calcium, since they have a suitable work function for electron injection into the electron transport layer. At the heart of the device there is the hole injection and transport layer (HTL), the doped emission layer (EML) consisting of an organic matrix doped with emissive molecules, and the electron injection and transport layer (ETL). More complex setups may contain additional protecting or blocking layers between the HTL, EML and ETL to prevent unwanted processes to take place that might decrease the efficiency of the device.[56]
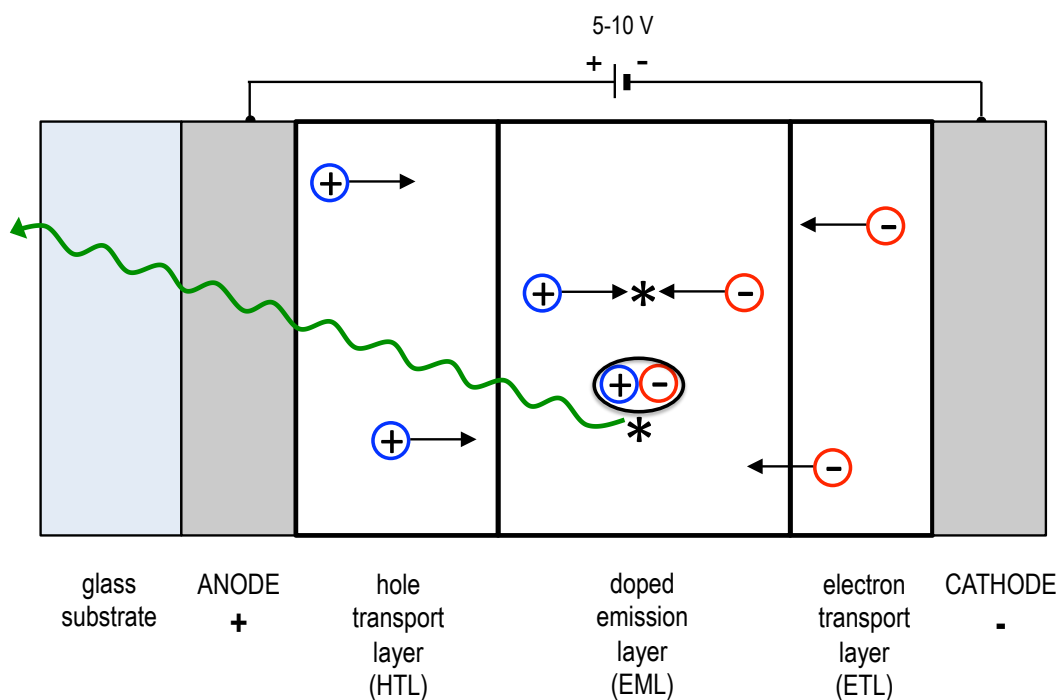

Figure 6. Schematic representation of the basic setup of a layered OLED structure. Electrons and holes travel in opposite directions recombining into an exciton on a doped emissive molecule (asterisk) which may relax by emitting radiation.

The operation of the OLED device is as follows. When a voltage is applied across the two electrodes, such that the anode has a positive voltage with respect to the cathode, an electric current flows through the device. Holes and electrons then travel across the layers in opposite directions. In particular, the electrons are injected from the cathode into the lowest unoccupied molecular orbital (LUMO) of the organic ETL and the holes are injected from the anode into the highest occupied molecular orbital (HOMO) of the organic material of the HTL. The energy levels of the materials composing the different layers must be chosen wisely so that adequate electron and hole transport takes place. Holes and electrons hop along the HOMOs and LUMOs of neighboring molecules along the HTL and ETL until they are brought together by electrostatic forces at the EML, where excitons are created. If the excitons are formed on the doping emissive molecules, an electronic excited state is populated which can relax radiatively by emitting light in the visible region.

Many different emissive materials can be used in OLEDs, but phosphorescent materials present clear advantages over fluorescent ones when it comes to triplet harvesting. For example, after the lowest triplet and excited singlet states of an emissive molecule are populated, emission of an organic molecule will mostly take place from singlet excitons by fluorescence due to the weak spin-orbit coupling (SOC) of light chemical elements. In an organometallic complex, SOC is very efficient due to the presence of the heavy metal, and so the triplet state may be populated directly from exciton formation on the emitter (triplet harvesting) or from the excited singlet state (singlet harvesting) by intersystem crossing (ISC). Emission can then take place from the lowest triplet state by phosphorescence. Therefore, the internal electroluminescence quantum efficiency of phosphorescent triplet emitters can in principle be up to four times higher than with fluorescent singlet emitters.[57]

2. Overview of the thesis

In this thesis, different organic and organometallic molecules with interest for optoelectronic applications have been studied from a computational standpoint. In particular, several organic dyes with suitable optical properties to be employed as sensitizers in DSSCs have been investigated. In a different direction, a series of phosphorescent Ir(III) complexes with potential application as emissive components in OLEDs have been also studied in detail. Finally, this thesis also includes the computational investigation of the photophysical properties of sulfur bridged naphthalene dimers, with potential application in organic photovoltaics (OPVs) and OLEDs.

The work presented in this thesis has been performed with different complementary goals:

1. To understand the fundamental features underlying the properties of the investigated photophysical processes from an electronic and atomic structure point of view.
2. To solve concrete aspects related to investigations at the experimental level by collaborating with other research groups. In particular, to understand the systems, rationalize the phenomena observed experimentally, give an answer to concrete questions arising from experimental characterization, and propose alternative or new systems with potentially improved properties.
3. To learn about the specific features and limitations of the methods of quantum chemistry used in the study of excited states and photophysical processes in molecular systems.

2.1 Fundamental aspects

A large part of the work presented in this thesis was conducted with the goal to comprehend the studied processes at a fundamental level. In the following, basic concepts which will appear throughout the manuscript will be discussed briefly.

2.1.1 Electronic states

In order to characterize the nature of an excited state, chemists take advantage of frontier molecular orbitals (MOs). Promotion of electrons between occupied and virtual orbitals leads to different excited states. Moreover, electronic states can be characterized by their symmetries. For example, in the case of an excited state dominated by a single configuration of an HOMO-to-LUMO transition, the spatial symmetry of the state is given by the direct product of the irreducible representations to which these two orbitals belong. These excited states can also exhibit different spin symmetries. In this thesis we have dealt

with singlet and triplet spin states. The ground state of the studied molecules was always a closed shell singlet, and low-lying excited singlet and triplet states have been systematically calculated and characterized.

The photoabsorbing state is usually known as the "optical" state. On the contrary, if a state has a negligible transition probability it is referred to as a "dark" state. When molecules have a well defined symmetry and belong to a given point group, it is straightforward to know, within the transition dipole approximation, which transitions will be symmetry forbidden, based on the irreducible representation of each state and the coupling operator, which is the electric dipole moment. When symmetry is not present, i.e molecules belonging to the C_1 point group, visualization of the molecular orbitals and their overlap can guide one to which may be the most intense transitions or the dark ones. Triplet and singlet states are however not coupled through the electric dipole moment since it does not operate on the spin variables. For these states to couple, an additional term must be included in the Hamiltonian, which is the spin-orbit coupling operator.

2.1.2 Photophysical processes

In the framework of molecular excited states, the principal photophysical processes are shown in Figure 7. Within the Born-Oppenheimer approximation, states are usually represented as parabolas along a given normal mode distortion. It is important to be aware that this picture is very simplified, since the potential energy surface (PES) will have 3N-6 dimensionality, where N is the number of atoms of the molecule. Nonetheless, this simplified representations turn out to be very useful when working in this field. In particular, because we always invoke the Franck-Condon (FC) approximation, which assumes that radiative transitions take place on a much shorter time scale than nuclear motion.[58] Therefore, these processes appear as straight lines in the diagram and the computed interstate energy difference for a frozen molecular geometry is know as the "vertical" transition energy. It is important to highlight that only photophysical processes have been studied in this thesis. In photochemistry, when reactions take place in electronic excited states, the picture can be more complex than that shown in Figure 7.

For a closed shell ground state, excited singlet states will be those mainly populated after photoabsorption, according to whether they are dark or optical states. After the molecule receives this excess of energy, it can then emit radiation after relaxing on the excited state

PES. Emission taking place from a singlet excited state is known as fluorescence, while from a triplet state is called phosphorescence. When calculating emission energies, we always assume that the molecule relaxes vibrationally to the minimum of the excited state and then the vertical radiative process takes place with a given probability.[58] However, before arriving to the minimum of the excited state PES it may encounter crossings with other states where non-radiative processes may take place. Internal conversion (IC) refers to non-radiative transitions between states of the same spin multiplicity and is governed by the derivative couplings.[59] These are vectors which represent those nuclear motions that allow two states of the same spin multiplicity to couple non-radiatively. On the other hand, intersystem crossing takes place between states of different spin-multiplicity, say a singlet and a triplet.[58] For this process to take place, the singlet and triplet states must coupled either via the SOC operator or through higher order terms (vibronic). All these processes will compete with emission and thus the final fate of the molecule will be governed by the relative rates of the different processes.
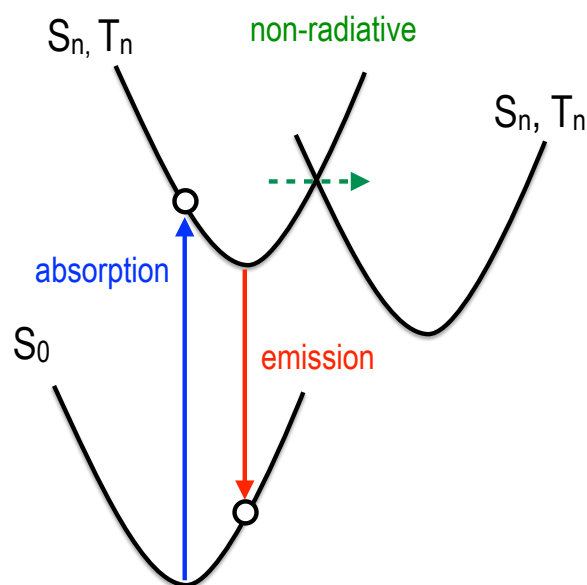

Figure 7. Schematic diagram of the ground and excited states with typical molecular photophysical processes studied in this thesis. Emission can be either fluorescent or phosphorescent, while the non-radiative transitions can be internal conversion or intersystem crossing.

An important rule that is commonly assumed is that proposed by Kasha,[60] which states that emission takes place from the lowest excited state of a given spin multiplicity. This is quite reasonable, since non-radiative decay between excited states is relatively fast because they lie close together in energy, so they will populate the lowest excited state before relaxing radiatively. Since the energy separation between the first excited state and the ground state

is larger than that among excited states, now emission can compete with non-radiative decay. In general, Kasha's rule holds except for some cases such as azulene,[58] where emission takes place from S_2, probably because of an exceptionally large energy gap between S_2 and S_1, and the existence of an S_1/S_0 conical intersection (CI) near the Franck-Condon region leading to efficient non-radiative decay from S_1.

This static picture of the PESs can be very powerful to predict which states will be relevant and which processes are prone to take place. In this framework, comparison with experimental data can be very useful to propose a mechanism to understand the experimental observations. However, dynamic simulations[61] are sometimes necessary to analyze the competition between different processes, although this approach is beyond the scope of the present work.

In this thesis, the photoabsorption of organic dyes has been investigated, which is one among the many complex processes taking place in DSSCs. For the Ir(III) complexes, the absorption and emission has been studied, and although non-radiative processes have not been explicitly investigated, we have rationalized their existence and potential physical origin mainly related to environment effects in solid or aggregated states. For the sulfur bridged naphthalene dimers studied in the last chapter, a Jablonski diagram of the photophysical processes has been proposed to interpret the experimental observations, taking into account radiative and non-radiative deactivation processes in the singlet manifold.

2.2 Presentation and structure of the thesis

The investigations presented in this thesis belong to molecular quantum chemistry and in particular to the investigation of the low-lying electronic excited states involved in the target photophysical processes. The majority of the studies have been done in collaboration with experimental partners. The combination of the information experimentalists can provide, together with the results obtained from electronic structure calculations carried out in the present thesis has been crucial for the interpretation of the observed data, as well as to get a deeper insight and a more realistic picture of the investigated properties.

Most of the results gathered in this manuscript have already been reported in several articles published in international journals. However, the thesis is not strictly presented as a

compendium of publications for several reasons. The principal one is to gain more flexibility in the format, and thus to have room to give a personal point of view on some of the subjects. Moreover, not all the work presented in this thesis has been published yet. There are also some results not included in the published papers that we have considered interesting enough to be included in this manuscript. Finally, as stated above, several of the published papers have emerged from collaborations with experimental groups, thus it seemed more suitable just to summarize the relevance of the experimental part at the beginning of each study presented in this thesis, so as to then focus here just on the work that I have done.

The thesis is divided in three broad chapters, each of them devoted to a specific topic. In each of them, a general introduction and the general objectives are outlined to contextualize the results that are presented afterwards. In addition, a general section on computational modeling is present in each chapter to explain the tools and methodologies employed to study each family of systems and reflect the knowledge related to each subject gained during the development of the thesis.

Chapter 1 is devoted to the study of the absorption process of several organic dyes with potential application in DSSCs. In particular, the influence of the nature of the π-bridge in donor-acceptor dyes has been investigated. The photophysical properties of the dyes are rationalized based on geometrical characteristics and their electronic structure. The charge transfer (CT) nature of the optical state has also been investigated with several computational tools. Solvent effects on the absorption of the dye have also been considered and simulated to give an explanation to experimental observations. One of the studies of this chapter was performed in collaboration with the group of Prof. Emilio Palomares at the *Institut Català d'Investigació Química* (*ICIQ*) in Tarragona (Spain) and the group of Prof. Peng Wang (*Chinese Academy of Sciences*, China).

Chapter 2 deals with phosphorescent Ir(III) complexes that have interest as triplet emitters for OLEDs. All the studies presented in this chapter have been done in collaboration with the experimental group of Prof. Inamur Rahman Laskar at the *Birla Institute of Technology and Science* (*BITS*) in Pilani, India, and his coworkers. After our first collaborations, we became interested in Ir(III) complexes exhibiting aggregation induced emission (AIE). This is a very interesting phenomenon where the emission intensity is enhanced in the

solid state compared to dilute solution. Systems presenting the AIE are very attractive for a wide range of applications other than OLEDs. In this chapter, a section is devoted exclusively to analyze the evolution of this field and the principal mechanisms proposed to explain this phenomenon. It does not pretend to be a complete review from the literature, but rather a critical assessment with personal thoughts on the subject. As for the results, we were interested to understand how the photophysical properties are influenced by the presence of different ligands on the Ir(III) complexes and by the presence of intermolecular interactions. The absorption and emission of the studied complexes has been characterized and different approaches have been taken to give an explanation to experimental observations from our partners.

In Chapter 3 a study on the photophysics of sulfur bridged naphthalene dimers is presented. This work was partially done during a research stay in the group of Prof. Mario Barbatti at the *Institut de Chimie Radicalaire* in Marseille (France). Herein we were interested in explaining the dependence of the photoluminescence (PL) of the aforementioned dimers on the oxidation state of the sulfur atom at the bridge. Experimental work on these compounds and related ones had been previously reported by the groups of Prof. Christopher J. Bardeen (University of California Riverside, USA) and Prof. Michael O. Wolf (University of British Columbia, Canada). An explanation for the different luminescence however was not given for the naphthalene dimers. We have tackled this problem by characterizing the excited states and crossings between the ground and first excited state PESs.

A significant part of the results presented in this thesis can be also found in the following scientific publications.

Chapter 1

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