

# Chapter 1

## Introduction

The solar cell architecture, developed in this work, takes advantage of a combination of hybrid solar cells and solid-state dye sensitized solar cells (ss-DSSCs), also called solid-state dye solar cells (SDSCs). Hybrid solar cells are based on a junction between an inorganic and an organic semiconductor, whereas the latter one is typically supposed to absorb the light, due to its higher absorption coefficient. This organic semiconductor has the additional duty to transport the light excitation energy in form of an electron hole pair (exciton) to the inorganic semiconductor, inject there an excited electron and transport the hole to the opposite side of the cell. Therefore, it ideally should have a high absorption coefficient and a high mobility and lifetime for the excitons and holes. As such organic all-rounders are rare and have not reached high efficiencies, yet, the ss-DSSC pursues another strategy: the separation of the functions onto different materials. Whereas the inorganic semiconductor keeps its function for transporting the electrons, the dye in DSSCs has no ability to transport excitons and holes. This is taken over by an additional organic material, the so-called: hole transport material (HTM). However, this is the other extreme, because the dye has no ability to transport excitons or charges. Consequently it needs a large area which controls its assembly to a monolayer by chemisorption in order to allow the contact of each dye molecule from two sides by different materials. This area is typically provided by a mesoporous  $\text{TiO}_2$  layer, which is covered by the dye monolayer and infiltrated by the HTM. Any aggregate formation of these dyes needs to be prevented and ideally also the random contacts between the dye molecules within the monolayer, because this leads to a fast quenching of the excitons. For an efficient exciton transport the dyes need to be orderly assembled, which can be achieved by a sophisticated functionalization for self-assembly. How to achieve this could be learned from natural early life forms, like bacteria, which made much more use of self-assembly compared to higher developed organisms like plants, which mostly employ proteins to assemble functional structures. Luckily some of these archaic species, like the photosynthetic active green sulfur bacteria, sustained their position in inhospitable niche regions, like near hot volcanic springs or in regions with the lowest light intensities on earth. Their light-harvesting system, also called

antenna system, demonstrates the potential of self-assembly to form highly ordered dye aggregates, which allow for an efficient exciton transport, and thus an efficient energy conversion in a smaller volume than needed for dye monolayers. Transferring this principle of self-assembly to artificial dyes might pave the way to improve conventional solar cells.

Light absorption is the first step of solar energy conversion. As the energy of solar radiation, i.e., the product of the number of photons and their energy, is maximal in the visible wavelengths range, all efficient solar cells absorb in this spectral region and thus are colored. Beside the intrinsically colored semiconductors, like silicon or the compound semiconductors for thin film solar cells, it is also possible to use optically transparent inorganic or organic semiconductors to construct solar cells by staining them with dyes. These so called dye sensitized solar cells (DSSCs) are typically based on the high bandgap semiconductor  $\text{TiO}_2$ , which is stained by a monolayer of an organic dye. The dye sensitizes the  $\text{TiO}_2$  for visible light, whereas otherwise the  $\text{TiO}_2$  would be only able to absorb and convert ultraviolet light to electricity. As organic dyes reach higher extinction coefficients as inorganic ones and are potentially cheap in manufacture, they are preferred candidates for low cost solar cells. Their current disadvantage of a reduced lifetime, reaching a couple of years, does not make them attractive for mass energy production, yet, but they have good chances to capture the market in niche applications like low cost solar cells for consumer electronics. There the lifetime of the solar cell is of less importance, because such electronics, like mobile phones or notebooks, are not intended for a many years long use, anyway. Additionally, such solar cells may also be replaced together with the battery, which is also accepted to have a life time limited to a couple of years. Furthermore the energy needed to manufacture solar cells based on organic dyes is much smaller than that needed for conventional inorganic solar cells. During the short lifetime of consumer electronics and in the weak light illumination conditions conventional solar cells might not be able to pay back the energy, which was used for their manufacturing. Thus, solar cells based on organic dyes are potentially better suited for consumer electronics and inorganic solar cells for roof-top applications.

Most conventional organic dyes can be applied to solar cells only in form of a monolayer, because their aggregates or multilayers do not reach a degree of ordering, necessary for an efficient energy transport over several dye molecules. To accommodate enough dye in form of a monolayer to absorb the full sunlight intensity, a large surface area is required. A high ratio of surface area to volume can be achieved with a very fine porous network like the mesoporous  $\text{TiO}_2$  used in DSSCs. As liquid electrolytes easily penetrate all pores and form a beneficial barrier preventing recombination at the interface to the  $\text{TiO}_2$ , such DSSCs achieve the highest efficiencies of all solar cells with organic components. However, the liquid electrolyte has certain disadvantages, like complicating the cell assembly and decreasing its long-term stability, due to sealing and leakage problems. Additionally, these solar cells need to be rigid, what increases their weight. Hence, the research effort to find solid-state alternatives for this electrolyte steadily increased within the last decade. However, not many solid (HTMs) exist, which

could infiltrate the small mesopores. Additionally, the recombination rate between the HTM and the  $\text{TiO}_2$  is around hundred times higher than with the liquid electrolyte. It was concluded therefore, that a more coarse-porous  $\text{TiO}_2$  structure would help to solve these problems, as it increases the pore size on one hand to facilitate the HTM infiltration and decreases the recombination affected surface/interface area on the other hand. This would be only possible in combination with dye multilayers instead of monolayers to accommodate enough dye on a smaller surface area. However, dye aggregates are only able to transport their excitation energy efficiently in form of excitons, when they are highly regular arranged next to another. As only very few dyes have been developed, which are able to self-assemble to such structures, Silviu Balaban examined the possibility to adopt the natural self-assembly principle to artificial dyes [1].

In this thesis, a biomimetic self-assembling dye, based on a zinc porphyrin, was investigated toward its suitability and applicability for solar cells. Previous investigations on this porphyrin showed the possibility to control the aggregate morphology and size to a certain degree within porous substrates by a two step process [2, 3]. Thereby, the porphyrin was first infiltrated from a solution in tetrahydrofuran (THF) into a mesoporous  $\text{TiO}_2$  layer containing additional macropores. The prevented self-assembly in this solvent allowed for an efficient infiltration, but led to the formation of amorphous aggregates. As this would not allow for efficient solar cells, a post-treatment in anhydrous *n*-heptane has been developed for a reorganization of the aggregates to the desired well-defined aggregates.

The aim of the present thesis was to better control the aggregate morphology and size in order to achieve a narrow distribution of these aggregate structures, and hence optoelectronic properties, and their micro- and macroscopic homogeneous implementation into solar cells. This thesis is therefore divided into two parts: the first one deals mainly with investigations on how the self-assembly could be controlled in order to achieve a homogeneous aggregate deposition with suitable optoelectronic properties. The second part is about the conception and construction of solar cell prototypes and their characterization.

## 1.1 Terms and Definitions

*Aggregate, self-assembly, crystal.* Aggregate is a generic term for solids regardless of their structure, which can range from a completely disordered (amorphous) one up to a highly regular ordered crystal. With the term self-assembly commonly a degree of spontaneous ordering is meant, which has a sophisticated growth mechanism or error correction mechanism during the crystal growth, which is often encountered in primitive natural organisms [4]. This may combine a fast growth rate with a low density of defects, due to an error correction mechanism, which effectively inhibits the further growth onto a misplaced unit. Self-assemblies combine more or less crystal properties, like a high degree of order, but typically

with a less extended long-range order, with additional properties such as an increased mechanical flexibility or tolerance for changes of the environmental conditions during the growth process, like the temperature.

*Chromophore, pigment, dye.* A chromophore (Greek: color-bearer) is originally the part of a molecule responsible for the color, but this term is commonly also used in a broader sense for relatively small entire molecules, like chlorophylls. These molecules may also be called pigments, though this term originally meant insoluble aggregates or particles. Dyes in the original sense are soluble chromophores with a specific functionality mostly for chemisorption onto certain materials, but this term is also used in analogy to chromophores.

*Exciton.* An exciton is an electron-hole pair, which originates typically by the absorption of light in organic materials. Whereas in inorganic semiconductors the excited electron is weakly bound to its remaining hole and dissociates very fast into separated charges, the binding energy of excitons in organics is much higher, typically between 0.5 and 1 eV [5]. Thus, excitons in organics normally dissociate only at suited interfaces to other materials, so-called hetero-junctions. Excitons can move between chromophores by the so-called Förster resonance energy transfer (FRET) or the Dexter energy transfer mechanism.

*Mesopore.* Mesopores are pores of an intermediate size between 2 and 50 nm. Smaller pores are called micropores and larger ones macropores [6]. This historic naming might be confusing as micropores might be associated with micrometer sized pores, what is not the case by this definition. The term nanopore is also used sometimes, instead of mesopore.

## References

1. Balaban TS (2005) Acc Chem Res 38:612–623
2. Marek PL, Sieger H, Scherer T, Hahn H, Balaban TS (2009) J Nanosci Nanotechnol 9:3708–3713
3. Marek P (2005) Selbstanordnende Zn-Porphyrine in makroporösen TiO<sub>2</sub>-Schichten für farbstoffsensibilisierte Solarzellen. Diploma thesis, Technical University of Darmstadt
4. Eigen M (1971) Naturwissenschaften 58:465–523
5. Brütting W (2005) Physics of organic semiconductors. Wiley-VCH, Weinheim
6. McNaught AD, Wilkinson A (1997) IUPAC. Compendium of Chemical Terminology, 2nd edn. (the "Gold Book"). Blackwell Scientific Publications, Oxford. XML on-line corrected version created by Nic M, Jirat J, Kosata B; updates compiled by Jenkins A: <http://goldbook.iupac.org>. doi:10.1351/goldbook, doi:10.1351/goldbook.M03853, ISBN: 0-9678550-9-8

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