Organic solar cells: Correlation between molecular structure, morphology and device performance

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To my parents

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I. List of Symbols

Å	Physical unit "Angström"
α	Molecular polarizability
β	Full width at half maximum (FWHM)
C	Crystallite dimension
χ	Vibronic wavefunction
D	Diffusion constant
Do	Dopant molecule
d	Distance
$E_{\rm A}$	Energetic position of the electronic state at the acceptor
$E_{\rm kin}$	Kinetic energy
$E_{\rm B}$	Coulomb binding energy
$E_{\rm pol}$	Polarization energy
$\dot{E_{\rm s}}$	Total electrostatic energy
$E_{\rm vac}$	Vacuum energy
e	Elementary charge/electron charge
$\varepsilon_{ m F}$	Fermi energy
ε_{o}	Vacuum pemittivity
$\varepsilon_{ m r}$	Relative dielectric constant
\mathbf{FF}	Fill factor (characteristics of a solar cell)
$F_{\rm D}$	Fluorescence spectrum of a molecule
h	Planck's constant
\hbar	$2\pi/h$
$\hbar \vec{k}$	Quasi momentum
$I_{\rm sc}$	Short circuit current (characteristics of a solar cell)
I_{D^*}	Ionization energy of an excited donor
J_0	Incident light intensity
$k_{\rm B}$	Boltzmann constant
$k_{\rm D}$	Exciton diffusion rate
$k_{\mathrm{DA}}^{\mathrm{F}}$	Förster transfer rate
$k_{\mathrm{DA}}^{\mathrm{D}}$	Dexter transfer rate
$k_{\rm nr}$	Rate of non radiative relaxation
$k_{ m r}^0$	Spontaneous emission rate in thermal equilibrium
K	Shape factor for the Scherrer equation

$L_{\rm ex}$	Exciton diffusion length
$L_{\rm o}$	Luminous intensity of an OLED
λ	Wavelength
M	Molecular mass
M_{A}	Matrix molecule
M_1	Specific light emission of an OLED
ν	Frequency
n	Density of free electrons
N	Avogadro constant
$N_{\rm A}$	Doping density
$\eta_{ m P}$	Power conversion efficiency of the solar cell (characteristics of a solar cell)
$\eta_{ m o}$	Luminous efficiency of an OLED
$P_{\rm max}$	Maximum electric power obtained from the solar cell
$P_{\rm L}$	Light intensity output of a OLED
p	Density of free of holes
R	Ohmic resistance
$R_{\rm s}$	Serial resistance
$R_{\rm p}$	Shunt resistance
$ ho_{ m v}$	Density of states
ρ	Density
P(E)	Normalized phosphorescence spectrum of a molecule
$\sigma_{ m A}$	Normalized absorption spectrum
$\sigma_{ m n}$	Conductivity of the elctrons
$\sigma_{ m p}$	Conductivity of the holes
au	Exciton lifetime
$ au_{ m e}$	Lifetime of electrons
T	Temperature
Θ	Bragg angle
$V_{\rm DA}$	Electronic coupling integral for excitation energy transfer
$V_{\rm oc}$	Open circuit voltage (characteristics of a solar cell)
W	Energy bandwidth
ξ	Diode ideality factor

II. List of Abbreviations

\mathbf{AM}	Air mass [*]
AO	Atomic orbital
BHJ	Bulk heterojunction
\mathbf{CT}	Charge-transfer
DA	Donor-acceptor
DOS	Density of states
$\mathbf{E}\mathbf{A}$	Electron affinity
\mathbf{ESP}	Electrostatic potential
\mathbf{ETL}	Electron transport layer
HOMO	Highest occupied molecular orbital
\mathbf{HTL}	Hole transport layer
HJC	Heterojunction
IP	Ionization potential
IPCE	Incident-photon-to-current efficiency
LMEC	Ligand-metal exchange coupled states
LUMO	Lowest unoccupied molecular orbital
MO	Molecular orbital
MPc	Metal phthalocyanine
MR-CI	Multi-reference configuration interaction
MPP	Maximum power point
OLED	Organic light-emitting diode
PSE	Photoelectron spectroscopy
\mathbf{PV}	Photovoltaic
DSC	Dye-sensitized solar cell
\mathbf{sDSC}	Solid state dye-sensitized solar cell
\mathbf{UPS}	Ultraviolet photoelectron spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	Single crystal X-ray diffraction
XRPD	X-ray powder diffraction

 * On the next page the term air mass (AM) is explained.

The air mass (AM) is a relative measure in astronomy of the pathlength l which light of a shining object (e.g. the sun) has to travel through the atmosphere to the ground. It is defined as the ratio of the path l and the minimum length l_0 at normal incidence:

$$AM = \frac{l}{l_0} \; .$$

If the light reaches the earth's surface under a certain zenith angle ς , the air mass can be approximated by

$$AM = \frac{1}{\cos(\varsigma)} . \tag{II.1}$$

Since the solar spectrum and accordingly the power conversion efficiencies of solar cells depend on the incident angle of the sunlight, these values vary with the position on earth where they are measured. Therefore, standardized solar simulators which simulate an AM 1.5 spectrum of the sunlight are used for solar cell characterizations. An AM 1.5 spectrum corresponds to the sunlight spectrum measured at an incident angle of the sunlight of 48° relative to the vertical on earth (see Eq. (II.1)).

III. List of Compounds

4,4'-bis[N-(1-naphthyl-1)-N-phenylamino]biphenyl
Tris-(8-hydroxyquinoline) aluminum
1,8(11),15(18),22(25)-Tetraanthracenyl zinc phthalocyanine
Silver
Aluminum
Titanium dioxide
4,7-diphenyl-1,10-phenanthroline
2,3-di(N-phthalimido)-5,6-dicyano-1,4-benzoquinone
Copper phthalocyanine
Buckminster fullerene
Iron phthalocyanine
2-[4-(dicyanomethylene)-2,3,5,6-tetrafluoro-1-cyclohexa
-2,5-dienylidene]propanedinitrile
Fluorine-doped tin oxide
Indium tin oxide
Lithium fluoride
1,8(11),15(18),22(25)-Tetranaphthyl zinc phthalocyanine
Nickel phthalocyanine
1,8(11),15(18),22(25)-Tetraphenyl zinc phthalocyanine
Silicon
2,2',7,7'-tetrakis (N,N-di-p-methoxyphenylamine)- $9,9'$ -spirobifluorene
Tungsten oxide
Zinc phthalocyanine

In the following the molecular structures of these organic compounds are shown.







F₄TCNQ







Bphen

Spiro-MeOTAD

A-ZnPc

Antracene







Figure III.1.: Molecular structures of compounds used and discussed in this work.

IV. List of Publications and Patents

IV.1. Publications in reviewed journals

- "Efficient organic tandem cell combining a solid state dye-sensitized and a vacuum deposited bulk heterojunction solar cell", I. Bruder, M. Karlsson, F. Eickemeyer, J. Hwang, P. Erk, A. Hagfeldt, J. Weis and N. Pschirer, Sol. Energy Mater. Sol. Cells 93(10), 1896-1899 (2009).
- "Influence of the molecular polarizability of novel zinc phthalocyanine derivatives on the device performance of organic heterojunction solar cells", I. Bruder, A. Ojala, C. Lennartz, S. Sundarraj, J. Schöneboom, R. Sens, P. Erk and J. Weis, *Sol. Energy Mater. Sol. Cells* 94, 310-316 (2010).
- "What determines the performance of metal phthalocyanines (MPc, M = Zn, Cu, Ni, Fe) in organic heterojunction solar cells? A combined experimental and theoretical investigation", I. Bruder, J. Schöneboom, R. Dinnebier, A. Ojala, S. Schäfer, R. Sens, P. Erk and J. Weis, Organic Electronics (2009) doi:10.1016/j.orgel.2009.11.016.
- "A novel p-dopant with low diffusion tendency and its application to organic light-emitting diodes", I. Bruder, S. Watanabe, J. Qu, I. B. Müller, R. Kopecek, J. Hwang, J. Weis and N. Langer, *Organic Electronics* (2010) doi: 10.1016/j.orgel.2009.12.019.

IV.2. Patents

IV.2.1. Pending and Published

- 1. "Photovoltaische Tandem-Zelle", Publication number of the international patent application: WO 2009/013282.
- 2. "Verwendung von halogenierten Phalocyaninen", Publication number of the international patent application: WO 2009/056626.

IV.2.2. Pending

1. "Mischungen, enthaltend Merocyanine, zur Herstellung von organische Solarzellen".

- 2. "Neue-Dicyano-benzoquinon-Derivate und deren Verwendung als Dotierstoffe in der organischen Elektronik".
- 3. "Substituted Phthalocyanines compounds for use in organic solar cells".

1. Introduction

1.1. Motivation

The world's hunger for energy is growing. To provide mankind with sustainable and ecofriendly energy is one of the major challenges of the 21st century - similar to the request for food by the end of the 19th century. As depicted in Fig. 1.1, the projections of world energy demand by the US Energy Information Administration forecasts a total growth from todays 14 TW towards 25 to 30 TW in 2050. Today industrial countries use about half the world's energy. Developing countries as e.g. China and India are responsible for the largest growth. Their demand will nearly be equal to industrial countries in 2025.

Thus, huge efforts must be undertaken to supply the additional energy demand in the future. To meet a demand of 14 TW by electrical power would require $14,000 \ge 1$ GW power plants¹. This means, that every day for the next 40 years a 1 GW power plant has to be built somewhere in the world.

The current primary energy source mix contains 85% fossil, causing emission of



¹Big stone coal power plants have usually a power output in the 1 GW range.

Figure 1.1.: Projections of world energy demand by the US Energy Information Administration.

greenhouse gases and being vulnerable to geopolitical constraints. With respect to the ecologic problems and the limited availability of fossil and nuclear fuels, special focus is on renewable energy sources to contribute significantly to the world's energy supply. However, in a best case the accessible capacities of water, wind, biomass and geothermal energy could just supply 22 TW in total (see Fig. 1.2). On the other hand, the sun's total capacity of 120,000 TW dwarfs all other energy sources. In total 36,000 TW are shining onto land. Assuming an efficiency of 25%, a solar cell covered area of 367 km x 367 km in the Sahara desert would meet the global energy demand in 2050. Just for comparison: This area represents only 0,3% of the Sahara which has a surface of about 9 million km²! Hence, the sun could be a singular solution to all our future energy needs if we knew how to harvest sun light in a cost-efficient way, which is not realized today.

Far from it, solar photovoltaic energy is presently the most expensive of all renewable sources. The average cost of photovoltaic generated electricity in middle Europe, Japan and in the US is about 35 \$/kWh. In areas with high solar radiation, e.g. Southern California or Spain, the same PV installation can harvest more than twice the amount of power compared to e.g. northern Germany. In these areas photovoltaic electricity prices come close to todays consumer electricity price level. As a consequence, in order to reach a competitive position in general, PV costs must be reduced further - at least by a factor of two.

One way to approach this goal could be the development of efficient organic



Figure 1.2.: Graphical representation of the additional global energy demand in comparison to the energy which can be provided by water, wind, biomass, geothermal and solar power. The volumes of the cubes are proportional to the respective energy amount.

solar cells, since the advantage of organic solar cells as compared to inorganic solar cells lies not in high efficiency but is founded rather on the expected low production costs.

1.2. Overview of organic solar cell concepts

Since the photovoltaic effect in organic solids was first observed 1959 in anthracene crystals [1], three main soild state device concepts have been emerged:

• Organic solar cells based on vacuum deposited small molecules This device concept is based on the thermal evaporation of at least two nand p-conducting materials. Excitons are generated due to the absorption of light in the respective organic materials. These excitons have to travel to an interface between the n- and p-conducting layer (the p-n junction) where - due to the present energetical conditions - they are splitted into free electrons and holes. Finally the respective charge carriers are transported towards their electrodes. As shown in Fig. 1.3a and Fig. 1.3b, p-n junctions can be realized as heterojunctions or as well as interpenetrating networks also called bulk heterojunctions.

For the fabrication of the first small molecule organic solar cells, chlorophylllike low molecular weight dyes based on phthalocyanines and porphyrins were used [2]. Since Tang [3] presented a 1% efficient bilayer heterojunction solar cell based on copper phthalocyanine (CuPc) and a perylene tetracarboxylic derivative (PTCBI) in 1986, enormous progress was made in research. The introduction of bulk heterojunction [4, 5] and tandem device architectures [6, 7, 8, 9] led recently to devices with power conversion efficiencies close or even higher than $\eta = 6\%$.

The fabrication under high vacuum is the main advantage and unfortunately also the main disadvantage compared to the two other device concepts which are described afterwards: The well defined fabrication environment ensures a very high reproducibility of the devices. Unfortunately, high vacuum technology is very expensive and complex to handle which is a disadvantage towards commercialization.

• Polymer based organic solar cells

The device architectures of polymer solar cells are similar to those used for small molecule cells shown in Fig. 1.3a and 1.3b. However, the fabrication differs significantly: Since polymers have a very high molecular weight, they can't be thermally evaporated. In contrast to small molecule based organic solar cells, heterojunction and bulk heterojunction polymer cells are therefore solution processed.

Semiconducting polymers such as P3HT (poly(3-hexylthiophene)) in combination with the fullerene C₆₀ are used for the fabrication of organic solar



Figure 1.3.: (a) Device setup of a heterojunction solar cell. A pconducting material forms a heterojunction with an n-conducting material in such a way, that exciton dissociation into free charge carriers is energetically favorable. (b) Device setup of a bulk heterojunction solar cell. Here the simple heterojunction is enhanced at the interface area by an interpenetrating network of n- and p-conducting materials.(c) Schematic structure of a dye-sensitized solar cell. In this cell concept, a mesoporous nanocrystalline TiO₂ film is attached to a transparent electrode. The particles in the TiO₂ film are covered by a monolayer of dye. The counter electrode is contacted through a liquid electrolyte or a p-conductor which penetrates the pores of the TiO₂ network.

cells since 1992 [10]. They have reached power conversion efficiencies of up to 5% in recent reports [11, 12]. Deposition of organics by screen printing, doctor blading, inkjet printing, and spray deposition is possible because these materials can be made soluble in contrast to the small molecule based organic solar cells. Additionally, these deposition techniques all work at low temperature, which allows devices to be fabricated on plastic substrates for flexible devices. Since polymer solar cells can be fabricated under ambient conditions, no expensive vacuum technology is needed which is another advantage towards commercialization.

• Dye-sensitized solar cells also known as Grätzel cells

Another cell concept is the dye-sensitized solar cell shown in Fig. 1.3c. This concept has attracted wide attention since its invention in 1991 by M. Grätzel [13]. In contrast to the upper shown device concepts, dye-sensitized solar cells are based on a mesoporous nanocrystalline TiO₂ film which is attached to a transparent FTO electrode. The particles in the TiO₂ film are covered by a monolayer of dye. The counter electrode is contacted through a liquid electrolyte or an organic p-conductor which penetrates into the pores of the TiO₂ network. When a dye molecule is excited by light, it injects one electron into the TiO₂, creating a positively charged dye molecule. This phenomenon produces the charge separation required for a photovoltaic cell. The electrons are donated from the counter electrode via the electrolyte to the positively charged dye on the TiO₂ surface, returning the dye molecules to their original state.

Soon laboratory scale efficiencies of over 10% were reported [14] with this device type. Due to the potential for low production costs, considerable efforts have been increasingly undertaken to enable a commercial up-scaling of this type of organic solar cell. Till today dye-sensitized solar cells provide the highest efficiencies of all organic solar cell concepts. Analogue to the polymer cells, also the dye-sensitized solar cell can be fabricated under ambient conditions. Unfortunately, the TiO₂ needs a heat treatment during the fabrication process which makes it difficult to realize this device concept on flexible foils. The use of liquid electrolytes is still an unsolved problem towards a longterm stability of these cells.

All organic systems are characterized by a high absorption coefficient: To absorb $\approx 90\%$ of the incoming light an organic dye layer has to be only 100 nm thick. For the same absorption, the thickness of a crystalline silicon needs to be ≈ 200 μ m. To compare the development of the power conversion efficiencies of organic solar cells with existing technologies based on inorganic materials, an overview provided by the **National Renewable Energy Laboratory** (NREL) is given in Fig. 1.4.



Figure 1.4.: Development of the power conversion efficiencies of different solar cell technologies. This graph is provided by the NREL (http://www.nrel.gov/solar/).

1.3. Overview of the thesis

The main task of this thesis was the investigation of novel molecular² and device designs which may lead to an improvement of the power conversion efficiency of organic solar cells. This topic was tackled at various levels. It was addressed by asking

- 1. Basic questions such as...
 - ... what is the physical origin of the different performance of metal phthalocyanines (MPc, M = Zn, Cu, Ni, Fe) in organic solar cells?
 - ...what is the influence of the molecular polarizability on the performance of organic heterojunction solar cells?
- 2. *Applied physical questions* such as how one could reduce the diffusivity of organic dopants within organic layers?
- 3. *Engineering and design questions* such as what about new organic solar cell concepts?

The thesis is structured in the following way:

In Chapter 2, basics of the physics of organic materials that are essential for the further discussion are reviewed. At first, an overview of the characteristics of aromatic molecules and organic molecular crystals is given. Next, the charge carrier transport in organic solids will be described. The transport mechanism in organic semiconductors is of much more complex nature compared to inorganic systems, due to the polaronic nature of charge carriers. In contrast to inorganic systems, strongly bound Frenkel excitons are created after light absorption in organic solar cells. Several mechanism by which an exciton may travel through an organic solid will be discussed. Finally, the basic principles of doping organic semiconductors will be reviewed.

In **Chapter 3**, the basic physics of organic solar cells based on small molecules will be discussed. At first, the operational principle and thus the consecutive fundamental steps of operating a photovoltaic device are described. Next, the heterojunction and bulk heterojunction device concepts will be introduced. The charge carrier separation and the loss mechanism in organic solar cells, based on charge carrier recombination, will be reviewed. Equivalent circuits for solar cells are introduced to describe the current-voltage characteristics in photovoltaic devices. Finally, the directly measurable parameters of a photovoltaic cell are introduced: The short-circuit current $I_{\rm sc}$, the open circuit voltage $V_{\rm oc}$, the fill factor FF, the power conversion efficiency $\eta_{\rm p}$ and and the incident photon-to-current

²All novel synthesized molecules were tested in heterojunction solar cells due to the easy, defined and reproducible fabrication of this device architecture.

efficiency IPCE.

In **Chapter 4**, organic processing technologies used in this work are reviewed. The principles of device fabrication, starting from the substrate design to the material processing by spin-coating and/or thermal vacuum evaporation, are briefly reviewed and explained. The current-voltage (IV) measurement setup is explained. Furthermore, the basics of material purification, ultraviolet and X-ray photo electron spectroscopy which were used within this work will be introduced and discussed.

In Chapter 5, an investigation on a metal phthalocyanine (MPc) series (M = Zn, Cu, Ni, Fe) targeted at a fundamental understanding of the physical origin of their different performance in organic solar cells will be presented. For these investigations MPc/C₆₀ based bilayer heterojunction (HJC) devices were built and analyzed. The crystal structure in thin films of the respective MPc's were explored by high resolution XRPD and AFM measurements and compared to powder data. The excited states of the respective MPc's were investigated by quantum mechanical calculations. The implications of the investigated effects on exciton diffusion are discussed and related to device performance.

In Chapter 6, the influence of the molecular polarizability α on the open circuit voltage $V_{\rm oc}$ of organic heterojunction solar cells is investigated. Therefore, novel zinc phthalocyanine (ZnPc) derivatives were synthesized having phenyl, naphthyl or anthracenyl groups attached to basic ZnPc cores. Since the influence of α on the Coulomb interaction of charges depend on the molecular arrangement of the respective molecules, the respective single crystal structures were solved by high resolution XRD. Based on the solved structures, quantum mechanical calculations of the charge separation mechanism were performed on model systems. The implications of the observed electronic effects is discussed and related to the device performance.

In Chapter 7, the diffusivity of organic dopants will be discussed. A novel p-dopant, 2,3-di(N-phthalimido)-5,6-dicyano-1,4-benzoquinone (BAPD) was synthesized and compared to the state-of-the-art dopant F_4TCNQ . The efficiency of the host-to-dopant electron transfer as well as the diffusion characteristics of the p-dopants were investigated by ultraviolet photo emission spectroscopy (UPS) and X-ray photo emission spectroscopy (XPS). Since the functionality of the dopants were investigated in OLED's instead of solar cells for technical reasons, a brief introduction in the setup and working principle of organic light emitting diodes will be given directly in this chapter.

In Chapter 8, a novel organic tandem solar cell architecture combining a solid state dye-sensitized cell with a $\text{ZnPc}/\text{C}_{60}$ based, vacuum deposited bulk heterojunction solar cell is introduced. Due to an effective serial connection of

both subcells and to the complementary absorption of the dyes used, a power conversion efficiency of $\eta_{\rm p} = (6.0 \pm 0.1)\%$ was achieved under simulated 100 mW/cm² AM 1.5 illumination. This power conversion efficiency is among the three highest achieved so far with organic solar cells including vacuum deposited small molecules.

In Chapter 9 and Chapter 10 an english and german summary is given, respectively.

The **Appendices** contain additional experimental and theoretical details which were not presented in the respective chapters due to clarity reasons.

2. Physics of organic semiconductors

Basics concerning the physics of organic semiconductors, that are essential for the further discussions, are reviewed in this chapter.

2.1. Aromatic molecules

The valence electrons of carbon atoms in molecules having conjugated π -electron systems are sp²-hybridized: As depicted in Fig. 2.1, the characteristic spatial electron distribution leads to an overlap of the p_z as well as of the sp^2 orbitals of adjacent carbon atoms resulting in molecular π - and σ -bonds, respectively. Thus, aromatics are planar, cyclic molecules with conjugated double bonds. During the transition from the atom to the molecule, the p_z atomic orbitals split into a bonding (π) and anti-bonding (π^*) orbitals which are energetically separated within a few eV. The energetically highest occupied bonding orbital in organic semiconductors is called highest occupied molecular orbital (HOMO). Congruently, the energetically lowest unoccupied anti-bonding orbital - usually indicated as the π^* orbital - is called LUMO.

The electronic excitation with the lowest energy is therefore taking place as a electronic $\pi - \pi^*$ excitation¹. Due to the energy gap in aromatic systems, these materials could absorb or fluoresce in the visible, near infrared or near UV spectral range and are therefore predestinated for the use in photovoltaic or light emitting applications.

2.2. Molecular crystals

Similar to atoms, molecules could also form single crystals, poly crystals or glasses. These structures are called organic solids. The solid state characteristics of organic crystals are mainly determined by the π -electrons [15]: The overlap of π -orbitals of two molecules in organic crystals allows the exchange of electrons and therefore charge carrier transport. The low symmetry of organic molecules often leads to crystal structures with low symmetry. This goes along with an anisotropy of macroscopic properties such as the optical absorption or the charge carrier mobility, which is characteristic for many organic systems. Molecular crystals

¹The notation $\pi - \pi^*$ describes the excitation of an electron from the π into the π^* orbital.

differ significantly from conventional solids, such as covalent or ionic crystals, in their optical, electrical and mechanical properties [16]. It has been shown, that within many organic crystals, e.g. phthalocyanine crystals, the individual molecules are clearly separated [17, 18, 19]. In the regions between the molecules, the electron density is very low. Thus, the crystal structure is usually formed by Van-der-Waals forces. These so called dispersion forces (London forces) are based on the electrical interaction between fluctuating multipole moments of the molecules. For non-polar neutral molecules the empirical Lennard-Jones potential is often used to describe these dispersion forces:

$$V_{\rm LJ} = \frac{A}{r^{12}} - \frac{B}{r^6} \,. \tag{2.1}$$

Here r is the distance between the molecules. A and B are material specific constants, describing repulsive and attractive molecular forces, respectively. Due to the weak intermolecular Van-der-Waals interaction, whose binding energy is much lower than covalent or ionic bonds, most organic solids have low melting and boiling points, as well as a small dielectric constant and a low charge carrier mobility.

These characteristic properties influence the performance of the respective materials in organic optoelectronic devices. Since anthracene is one of the most investigated organic semiconductors and silicon is the prominent inorganic equivalent, these materials were chosen to demonstrate the differences of the most important physical characteristics of organic and an inorganic semiconductors. The comparison is shown in Table 2.1.



Figure 2.1.: sp²-hybridization of the valence electrons of two carbon atoms lead to molecular π - and σ -bondings.

Properties	Silicon	Anthracene
Molecular weight [g/mol] Melting point [°C] Density [g/cm ³] Relative dielectric constant Electron mobility at 300 K [cm ² /Vs] Hole mobility at 300 K [cm ² /Vs]	$28.08 \\ 1414 \\ 2.32 \\ 11,7 \\ 1400 \\ 450$	178.22 217 1.28 3,2 ≈ 1 ≈ 1

Table 2.1.: Physical characteristics of anthracene and silicon [20]. The electron and hole mobilities are usually anisotropic in organic as well as in inorganic crystals. Thus, the shown values are only valid in one direction (see [20]).

2.3. Charge carrier transport in organic solids

For the description of inorganic semiconductors usually the "band-theory" developed 1926 by Felix Bloch is used. The theory is based on the translation symmetry of the crystal. The lattice periodicity (expressed by the periodic potential $V(\vec{r} + \vec{R}_n) = V(\vec{r})$ with the counter *n* and the lattice vector \vec{R}_n) enforce, that the solutions of the single-electron Schrödinger equation

$$H(\vec{r})\psi_{\vec{k}}(\vec{r}) = \left(-\frac{\hbar^2 \nabla^2}{2m} + V(\vec{r})\right)\psi_{\vec{k}}(\vec{r}) = E(\vec{k})\psi_{\vec{k}}(\vec{r}) , \qquad (2.2)$$

comply with the Bloch condition [21]

$$\psi_{\vec{k}}(\vec{r} + \vec{R}_n) = e^{(i\vec{k}\vec{R}_n)}\psi_{\vec{k}}(\vec{r}) .$$
(2.3)

Here m is the free electron mass and $\hbar \vec{k}$ the quasi momentum.

The strong overlap of the respective atomic orbitals (AO) within inorganic semiconducting crystals usually lead to broad bands. The movement of charge carriers within these bands can be described by Bloch waves. In contrast, the molecular orbitals (MO) in organic semiconductors overlap only weakly (*vide supra*). This results in an only slightly increased width of the respective MO's which could form only narrow bands. Thus, charge carriers in organic semiconductors are more localized and interact therefore strongly with the present electronic and nuclear subsystems. This phenomena are too complex to be described by many-particle methods, and are often dealt by phenomenological approaches.



Figure 2.2.: (a) The overlap of molecular orbitals (MO's) in organic semiconductors lead to a formation of bands with a width W. (b) If the LUMO of a molecule is occupied by an electron, the charge interacts strongly with the adjacent electronic and nuclear subsystems. Thus, the system could relax energetically by the polarization energy $E_{\rm pol}$. An overlap of the MO's of these localized- or polaronic-states could lead to the formation of polaron bands. It is obvious that influence of holes, occupying the HOMO of a molecule, are described similarly.

2.3.1. Hopping or band transport in organic semiconductors?

In organic semiconductors, the charge carriers can be effectively localized on a single molecule due to their weak electronic coupling. Because of their limited spatial extent, the carriers polarize the surrounding lattice which relaxes to accommodate the extra charge. The carriers are hence accompanied by a lattice deformation, resulting in a new entity called polaron [16]. Because polarons in organic crystals are localized only on a few molecules, they are called small polarons. As depicted in Fig. 2.2, the formation of localized states in organic semiconductors is determined by the ratio of the polarization energy $E_{\rm pol}$ to the bandwidth W: If W is significantly smaller than the polarization energy $E_{\rm pol}$

$$W \ll E_{\rm pol}$$
 (Condition for polaron generation), (2.4)

charge carriers will localize and form polarons and holons, respectively. Disordered molecular solids exhibit usually an inhomogeneous energy distribution of their localized transport states (see Fig. 2.3). Therefore, the charge carrier transport between adjacent molecules is thermally activated and the mobility increases with increasing temperature [22]. This kind of thermally activated charge carrier transport is called hopping transport. Sometimes the ensemble of localized states within a certain energy range is called band. It is stated here, that the term band in this context has nothing to do with energy bands in an ideal crystal.

In contrast also band-like conduction can occur in organic semiconductors: In well organized organic crystals, Bloch states can be created by a linear combination



Figure 2.3.: Schematic picture describing the hopping transport. Sometimes the ensemble of localized states within a certain energy range is also called band. The transport within these bands is thermally activated and has nothing to do with energy bands in an ideal crystal.

of the localized states which could form a polaron band². Thus, polarons can be treated as quasi-particles carrying the charge and occupying Bloch states, i.e. are characterized by \vec{k} and $E(\vec{k})$. Similar to inorganics, the conductivity in very pure and highly ordered organic solids is limited by scattering processes with phonons [23]. In contrast to the hopping transport, the conductivity is increasing with decreasing temperature due to a reduction of the respective scattering probability.

It can be summarized, that in well organized organic crystals the charge transport is based on polaron bands, while the hopping transport prevails in polycrystalline and amorphous materials.

2.4. Exciton transport in organic solids

In organic solar cells, molecules are electronically excited due to the absorption of light. This excited state is called exciton [16]. To be dissociated into charge carriers, the excitons have to travel towards an interface within the solar cell. It has been found, that the motion of excitons in organic solar cells is described best by a hopping based diffusion processes, characterized by a diffusion length L_D [15]. There exist several mechanism by which an exciton could travel through an organic solid:

1. Trivial energy transfer process

At intermolecular distances larger than 100 Å, this transfer process is of importantance. Here, photons are emitted by molecules due to fluorescence

²Due to the electron-phonon interaction and the associated higher effective mass, as well as due to the increased localization of charge carriers, the width of the polaron band is significantly smaller in comparison to the bandwidth without polarization effects.

or phosphorescence. In course, the energy of this photon can be absorbed by other molecule. This process is long range and may be important in certain cases such as laser structures with high finesse optical cavities.

2. Förster transfer

This energy transfer process is based on the dipole-dipole interaction between two molecules. In the case where the dephasing time τ_{ϕ} is long compared to the time of cycling between the photon emitting and photon accepting molecules, i.e. $J\tau_{\phi} \gg \hbar$, where J is the spectral overlap integral, the energy oscillates back and forth coherently at a frequency J/\hbar . In case of a coherent dipole-dipole interaction, J is proportional³ to R^{-3} . Thus, the rate k_{DA}^{F} of the energy transfer is [15]

$$k_{\rm DA}^{\rm F} \sim \frac{|J|}{\hbar} \sim \frac{1}{R^3} . \tag{2.5}$$

In the case of large molecules or molecular aggregates the dephasing time τ_{ϕ} is usually too short for coherent transfer because the electronic excitation is strongly coupled to a dense system of vibrational states. Here, the dephasing time is approximately $\tau_{\phi} \approx \hbar/\Delta E$ where ΔE is the vibrational bandwidth. Hence, only when $|J| > \Delta E$ coherent transfer occurs. In the incoherent regime $(|J| < \Delta E)$, the transfer rate is [15, 24, 25]

$$k_{\rm DA}^{\rm F} = \frac{1}{\tau_{\rm D}} \frac{1}{R^6} \frac{3}{4\pi} \int \frac{c^4}{\omega^4 n^4} F_{\rm D}(\omega) \sigma_{\rm A}(\omega) \, d\omega = \frac{1}{\tau_{\rm D}} \left(\frac{R_0}{R^6}\right) \,, \qquad (2.6)$$

where $\sigma_{\rm A}$ is the normalized spectrum of the photon absorbing molecule, $F_{\rm D}$ is the fluorescence spectrum of the photon emitting molecule, n is the index of refraction of the surrounding medium, c is the speed of light and $\tau_{\rm D}$ is the lifetime of the exited state of the photon emitting molecule. The integral in Eq. (2.6) can be represented by the material characteristic Förster radius R_0 . The transfer rate $k_{\rm DA}^{\rm F}$ is averaged over all possible relative orientations of the molecular dipoles which describes an isotropic system. After the excitation of the photon emitting molecule, the electronic excitation energy can be partly converted into excited vibrational states and is thus no longer available for the dipole-dipole interaction. This is reflected experimentally by a difference in the fluorescence and absorption spectrum described by Eq. (2.6). In order to have an effective Förster transfer process, the fluorescence and absorption spectrum of the respective molecules must overlap substantially. Furthermore, since the process occurs via dipole coupling, the transitions must be dipole allowed. In organic light emitting diodes where the emissive layer is doped with an fluorescent guest species, energy transfer from the host to the guest material occurs mainly through the Förster mechanism.

³The R^{-3} dependence is equivalent to the classical interaction of two static dipoles.

3. Dexter transfer

In contrast to the Förster transfer, dipole-forbidden energy transfer between two molecules takes place either through higher multipole interactions or by electron exchange. In the case of triplet excitons, electron exchange dominates the transfer rate. The transfer rate was calculated by Dexter as [15]

$$k_{\rm DA}^{\rm D} = \frac{2\pi}{\hbar} \left| \beta_{\rm DA}^2 \right| \int P_{\rm D}(E) \sigma_{\rm A}(E) \ dE \sim e^{(-2R/L)} \cdot J \ , \tag{2.7}$$

where β_{DA} is the exchange interaction energy, L is the intermediate orbital radius of the involved molecules and J is the overlap integral $\int P_{\text{D}}(E)\sigma_{\text{A}}(E) dE$ of the respective normalized phosphorescence $P_{\text{D}}(E)$ and absorption spectra $\sigma_{\text{A}}(E)$ of the two interacting molecules. Due to the exponential dependence, a strong decay of the Dexter transfer with the distance is given.

2.5. Doping fundamentals

Controlled doping of inorganic semiconductors was a key step for today's electronic device technology. The realization of n- and p-conducting semiconductors was crucial for the realization of stable pn-junctions, the basic building block of all electronic devices.

The basic principles of doping in organic semiconductors are similar to those in inorganic materials: Mobile carriers are generated by exciting electrons from donors into a conduction band or by capturing electrons with acceptors and thus creating holes in a valence band. In organics, one has to add constituents, which either donate electrons to the lowest unoccupied molecular orbitals (LUMO, ntype doping) or remove electrons from the highest occupied molecular orbitals (HOMO) to generate holes (p-type doping) (see Fig. 2.4). These constituents can be of inorganic nature such as the acceptors tungsten oxide (WO₃) or lithium fluoride (LiF) as well as of organic nature represented by small and reactive molecules such as the acceptor F_4TCNQ . Acceptors are negatively charged if occupied and neutral if empty, while donors are electrically neutral if occupied and are positively charged if empty. The p-doping process of an organic semiconductor may be described in two fundamental steps:

- 1. The initial charge transfer of an electron from a matrix molecule M_A to a p-dopant D_o leading to the formation of a intermediate local charge transfer (CT) state $\left[M_A^+D_o^-\right]$.
- 2. Dissociation of the CT-state into a quasi-unbound state by overcoming the attractive Coulomb interaction. This means, that the hole (holon) has to jump further onto the next matrix molecule M_A leaving behind the charged dopant D_o^- [26].



Figure 2.4.: Mechanism of molecular p- and n-type doping. (a) p-type doping: Initial charge transfer of an electron from a matrix molecule M_A to a p-dopant D_o . (b) Formation of a intermediate local charge transfer (CT) state $\left[M_A^+D_o^-\right]$. (c) n-type doping: Initial charge transfer of an electron from a n-dopant D_o to a matrix molecule M_A . (d) Formation of a intermediate local charge transfer (CT) state $\left[M_A^+D_o^+\right]$. Due to the Coulomb interaction, the energy levels of the transport states of the matrix molecule are shifted in (b) and (d), depending on the distance to the remaining charged dopant.

Thus, the positive charge (holon) can move through the organic layer by hopping and the density of M_A^+ determines the density p(T) of holons in equilibrium in the layer. Doping of M_A with D_o is efficient if the density p(T) of holons is thermally independent and increase linearly with the density N_A of the dopant. In this case the limit of shallow acceptors is reached. However, it has been shown [27, 28], that doping of organic semiconductors lead usually to the case $p(T) \ll N_A$ and that the density holons p(T) is thermally activated. Thus, the model of deep acceptors seems to be appropriate to describe the doping effect in organic molecular layers.

It is obvious that n-type doping may be described similarly.

3. Fundamentals of organic solar cells

In this chapter the basic physics of organic solar cells based on small molecules will be discussed. Furthermore, device properties will be evaluated concentrating on the short-circuit current $I_{\rm sc}$, the open circuit voltage $V_{\rm oc}$ the fill factor FF, and the power conversion efficieny $\eta_{\rm P}$.

3.1. Basic operational principle of polymer and vacuum deposited small molecule based organic solar cells.

In a classical inorganic solar cells, charge carriers - an electron and a hole - are generated by the absorbed sunlight. These two oppositely charged carriers are only weakly bound due to an efficient electrostatical screening based on the rather high dielectric constants ε_r in inorganic semiconductors. The electrostatic potential drop at the interface between a p- and an n-doped semiconductor layer (the pnjunction), leads to their separation and transportation to the respective contacts.

In organic semiconductors, things are somewhat different. Here, the screening of opposite charges is much weaker since the dielectric constant $\varepsilon_{\rm r}$ in organics is much lower. Therefore, optical excitations in an organic solid rapidly relax due to strong dielectric polarization effects and form excitons with binding energies $E_{\rm B}$ ranging from 0.1 eV to 2 eV [29]. These binding energies are huge compared to inorganic semiconductors as for example GaAs where an $E_{\rm B}$ of 4 meV was measured [30]. Thus, the conversion of light into current in an organic solar cell may be visualized (see Fig. 3.1) as taking place in four consecutive fundamental steps:

- 1. Absorption of light leading to the generation of strongly bound Frenkel excitons,
- 2. dissociation of the optically activated excitons into spatially separated but still bound positive and negative charges (polaron-holon pair generation),
- 3. selective transport of the polarons and holons through the bulk of the device to the respective collecting electrodes,
- 4. extraction of the charge carries at the electrodes.

As the strong interaction of the photo induced Frenkel excitons is more difficult to be overcome as compared to excitations in inorganic systems, the structure of organic solar cells has to be different compared to inorganic devices.

3.2. The concept of a donor-acceptor (DA) interface

The first organic solar cells were based on one active layer made of a single material embedded between two metal electrodes of different work functions. By the absorption of light, strongly bound Frenkel excitons were created. These have to be split in order to finally generate a photo current. The binding energy $E_{\rm B}$ can be overcome by ...

- ... a high intrinsic electric field,
- ... a high thermal energy $k_{\rm B}T$,
- ... dissociation at the metal contacts.

Unfortunately, these processes have a rather low efficiency: Under ambient conditions, the temperature is not high enough, and the sample thickness is usually much thicker than the exciton diffusion length $L_{\rm D}$. Furthermore, the present



Figure 3.1.: Operational principle of organic solar cells: (a) Creation of a Frenkel-exciton after light absorption. (b) Exciton diffuses towards a DA-interface where it dissociates into a polaron pair. (c) Diffusion of the charge carriers towards their respective contact electrodes where they can be extracted.

built-in fields are far to weak to split the strongly bound Frenkel excitons. The consequence: Excitons are mostly not dissociated, but recombine instead.

The introduction of donor-acceptor (DA) interfaces by implementing a second layer was a quantum leap in terms of power conversion efficiency of organic solar cells [3]. In these bilayer or heterojunction solar cells (see Fig. 1.3a or Fig. 3.1), the light is usually absorbed mainly in the so-called donor material which is made out of hole conducting small molecules. The photo generated Frenkel exciton can now diffuse within the donor towards the interface to the second material, the acceptor, which is usually strongly electronegative. A prominent example for an electron acceptor material is the buckminster fullerene (C₆₀). If the energy difference between the ionization potential IP_D of the electron donating material and the electron affinity EA_A of the electron accepting material is larger than the exciton binding energy E_B , exciton dissociation is energetically favorable (see Fig. 3.2):



$$IP_{\rm D}^* - EA_{\rm A} - E_{\rm B} < 0$$
 (Condition for exciton dissociation). (3.1)

Figure 3.2.: Schematic picture describing the exciton dissociation at a DA-interface: (1) HOMO_D and LUMO_D level of an uncharged not excited donor molecule. (2) An excited donor molecule is ionized by an energy $IP_{\rm D}^*$. (3) The electron is transferred ultrafast to the LUMO of an electron acceptor within a sub picosecond timescale by gaining the energy $EA_{\rm A}^+$. (4) Due to the Coulomb interaction between the electron on the acceptor and the remaining hole on the ionized donor, an additional energy barrier $E_{\rm B}$ has to be overcome for a spacial separation of the charge carriers. Thus, exciton dissociation is energetically favorable if $IP_{\rm D}^*-EA_{\rm A}-E_{\rm B} < 0$.

 $IP_{\rm D}^*$ is the ionization potential of the excited donor, $EA_{\rm A}$ the electron affinity of the acceptor and $E_{\rm B}$ the binding energy of the excitons in the donor (in absolute values, respectively). The charge transfer over such a DA-interface occurs very fast and very efficient [31]. With time resolved experiments, using femtosecond laser pulses, it was shown, that the dissociation process at the DA-interface takes place within a timeperiode < 100 fs. During the exciton dissociation the hole stays on the donor molecule while the electron is transferred on the acceptor molecule (see Fig. 3.2). Thus, the charge carriers are spatially separated. Even though residing on two separate molecules, which lead to a clearly lowered recombination rate (lifetime: micro to milliseconds) as compared to the Frenkel excitons (lifetime: nanoseconds), the positive and negative charges are still Coulomb bound. Therefore, a further step is necessary for the final charge pair dissociation.

3.3. Charge carrier separation in organic heterojunction and bulk heterojunction solar cells

To overcome the Coulomb attraction between the spatially separated but still bound polaron-holon pair an electric built-in field is needed. This dependence becomes manifest in the strongly field dependent photocurrent of organic solar cells: If the internal field, which is mainly determined by the influence of the different work functions of the metal electrodes, is too low, the so-called geminate recombination of the charge carrier pair is very probable [32]. The term "geminate" is used to indicate, that an electron recombines with exactly the same hole it was separated from before. If the field supported charge carrier separation is successful, polarons and holons can be transported towards their respective contacts, in order to generate a photocurrent. The limiting factor in the heterojunction concept is layer thickness of the absorbing material: For a full absorption of the incident light, the layer thickness of the absorbing material has to be in the order of the absorption length which is ≈ 100 nm. This is much more than the diffusion length $L_{\rm D}$ of the excitons [33, 34, 35, 36]. Thus, the potential of the heterojunction solar cell is difficult to exploit.

A further development of the heterojunction device concept was the so-called bulk heterojunction solar cell [37]. This device concept accounts for the low exciton diffusion length $L_{\rm D}$ in disordered organic semiconductors, as well as for the required thickness for a sufficient light absorption. This approach features a distributed junction between donor and acceptor material: As depicted in Fig. 1.3b, both components interpenetrate each other, so that the interface between them is not planar any more but spatially distributed. It is implemented by spincoating a polymer/fullerene blend or by co-evaporation of conjugated molecules. Bulk heterojunctions have the advantage of being able to dissociate excitons very efficiently over the whole extent of the solar cell because the generated excitons have
to overcome only a very short distance to the next DA-interface. Therefore, polaron pairs can be generated anywhere in the film. The disadvantage of the bulk heterojunction concept is the somewhat more difficult separation of the charge carriers due to the increased disorder. Thus, the percolation to the contacts is not always given in these disordered material mixtures and it is therefore more likely that charge carriers are trapped and recombine. However, the positive effects outweigh the negative. Today's most efficient organic solar cells are based on the bulk heterojunction concept [4, 5].

3.4. Use of the terms "donor" and "acceptor"

At this point it is worthwhile to note, that in contrast to inorganics the term "donor" and the term "acceptor" is used manifold in relation to organic solar cells. Thus, a donor can describe a molecule(material)

- 1. ...which emits a photon via relaxation from an excited state,
- 2. ...which transfers an electron to another molecule over an interface in a donor-acceptor (DA) system,
- 3. ...which acts as an organic n-dopant (similar to the inorganic dopants) and donates an electron into the LUMO of an organic semiconductor.

The respective issues of organic acceptors can be summarized equivalently.

3.5. Loss mechanism in organic solar cells

A prerequisite for a highly efficient conversion of photons into electrical current in an organic solar cell is an efficient dissociation of Frenkel excitons as well as an efficient extraction of charge carriers in an external circuit. As discussed in chapter 3.3, the problem of inefficient exciton dissociation could be solved due to the introduction of so-called bulk heterojunctions. However, charge carries can still be lost due to geminate and/or non-geminate recombination as well as by trapping on their way to the contact electrodes (see Fig. 3.3). For a high performance solar, all loss mechanism have to be minimized. Recombination processes can be distinguished in radiative recombination (fluorescence and phosphorescence), and non-radiative recombination by phonon creation. Since the recombination probability of charge carriers is mainly a material dependent property, the recombination problem has to be rather solved by an advanced molecular design and/or processing than by device engineering. In the following, the respective recombination processes are discussed.

Recombination is a reaction of an electron with a hole, in which the electron and the hole are annihilated [38]. In a radiative recombination process, a photon is emitted carrying momentum and energy. In non-radiative recombination, one or more phonons are created or absorbed, often mediated by states in the band gap caused by impurities. In each case the primary step is based on the fact, that electrons and holes find each other. Thus, the annihilation process can be described by a rate $r_{\rm e}$ which is proportional to the density n(T) and p(T) of the respective charge carriers:

$$r_{\rm e} \sim n(T)p(T) . \tag{3.2}$$

3.5.1. Non-radiative recombination

The energy of a recombining Frenkel exciton could end up in vibrations of atoms in the case of non-radiative recombination processes. These vibrations are quantised and could have energies in the order of 10 meV. This is much smaller than the binding energy $E_{\rm B}$ of an exciton, which is typically in the order of 0.1 eV to 2 eV [29]. Thus, many phonons must be generated simultaneously to take up the energy of an exciton. Therefore, non-radiative recombination is only predominant, if mediated by states in the energy gap of the organic semiconductor, since otherwise this process has a comparably small probability. These gap-states allow the recombination process to proceed stepwise with a smaller number of phonons simultaneously generated. This shows the importance of avoiding any imperfections, such as impurities and lattice defects, which give rise to states in the gap. However, at the metal contacts of an organic solar cell, states within the energy gap cannot be avoided. Metals have a continuum of states below and above the Fermi energy, which aligns with the Fermi energy of the adjacent organic semiconductor. As a consequence, these states could lie within the energy gap of the organic semiconductor and thus the non-radiative recombination probability at



Figure 3.3.: Schematic picture showing the different steps towards photo current generation (green) in organic solar cells. For a high performance solar, the loss mechanism (red) have to be minimized for all steps.



Figure 3.4.: Schematic picture showing the device setup and the respective transport levels of a typical $ZnPc/C_{60}$ heterojunction solar cell. As depicted, a thin (3 nm to 6 nm) Bphen layer is evaporated between the electron conducting C_{60} and the Ag-electrode. Bphen is a amorphous, wide band gap exciton blocking material which also effectively suppresses the penetration of Ag particles into the C_{60} . Due to the energetic positions of the respective transport level the electrons have to tunnel through this material in order to reach the Ag-electrode.

the interface is very large. One way to avoid excessive interface recombination at the contacts could be the reduction of the contact area. As depicted in Fig. 3.4, a more elegant and more effective elimination of interface recombination can be achieved, if electrons and/or holes could be kept at a distance from the metal contact interface. Thus, electron and/or hole blocking layers are used in real organic solar cells, in order to shield the photoactive area of a device from the metal electrodes.

3.5.2. Radiative recombination

Radiative recombination cannot be avoided without losing the ability to absorb light. Therefore, similar to inorganics this is the process which ultimately limits the performance of an organic solar cell. The rate of radiative recombination can be described by integration over all photon energies occurring in transitions between the edge of the LUMO and HOMO [39]

$$k_{\rm r} = \int \alpha(\hbar\omega) \frac{2\Omega n}{h^3 c^2} \frac{(\hbar\omega)^2}{\exp\left[\frac{\hbar\omega - (E_{\rm LUMO} - E_{\rm HOMO})}{k_{\rm B}T}\right] - 1} d(\hbar\omega) , \qquad (3.3)$$

where Ω is the dihedral angle, n is the index of refraction and $\alpha(\hbar\omega)$ is the absorption coefficient. If the band gap is smaller than the photon energy by several $k_{\rm B}T$, which is the case for long wavelength absorbing dyes used in organic solar cells, the -1 in the denominator can be neglected and a very simple relation results:

$$k_{\rm r} = k_{\rm r}^0 \exp\left(\frac{E_{\rm LUMO} - E_{\rm HOMO}}{k_{\rm B}T}\right) , \qquad (3.4)$$

where k_r^0 is the spontaneous emission rate in equilibrium with the 300 K surroundings, resulting from Eq. (3.3). In doing so, the absorption coefficient $\alpha(\hbar\omega)$ is assumed to have the same value under solar irradiation as in the dark, an assumption well justified at least for non-concentrated solar irradiation. Eq. (3.4) indicates, that the radiative recombination increases with an increasing band gap of the semiconductor, closing the gap to $\hbar\omega$.

3.6. Equivalent circuits for solar cells

Since a self-contained theory describing the current-voltage dependence in organic solar cells is still missing, one has to use equations describing originally inorganic devices. Despite the fact, that the photo current in organic solar cells is generated in a significantly different way compared to inorganic cells, the inorganic equations describe the current-voltage characteristics in the organic cells surprisingly good:

The current-voltage characteristic of an ideal solar cell can be described as the sum of the dark current of a diode [21]

$$I(V) = I_{\text{sat}} \left(\exp \frac{eV}{\xi k_{\text{B}}T} - 1 \right)$$
(3.5)

and the photo current, contributing

$$I(\mathbf{V}) = -I_{\rm ph}.\tag{3.6}$$

Here, I_{sat} is the diode saturation current and ξ is the diode ideality factor. The ideality factor is derived to 1 by semiconductor theory. However, it has been found empirically, that real diodes deviate from the ideal diode relation ($\xi = 1$). Thus, the ideality factor has been introduced. In silicon based diodes ξ was found to vary between 2 for low currents and 1 for high currents. Adding up Eq. (3.5) and Eq. (3.6) leads to

$$I(V) = I_{\text{sat}} \left(\exp \frac{eV}{\xi k_{\text{B}}T} - 1 \right) - I_{\text{ph}}$$
(3.7)

Eq. (3.7) is the standard solar cell equation. It leads to the equivalent circuit of an ideal solar cell sketched in Fig. 3.5. This consists of an ideal diode and a current source in parallel. The simplest extension to a real device, operation in a stationary state, consists in introducing losses via a series resistance $R_{\rm s}$ and a parallel resistance $R_{\rm p}$ (Fig. 3.6). $R_{\rm s}$ represents contact resistances such as ohmic losses in the front and rear contact. $R_{\rm p}$ includes any current bypassing the DAinterface as well as shunt currents through shorts. Based on Eq. (3.7) this leads to

$$I(V) = -I_{\rm ph} + I_{\rm sat} \left(\exp \frac{eV_{\rm p}}{\xi k_{\rm B} T} - 1 \right) + \frac{V_{\rm p}}{R_{\rm p}}.$$
 (3.8)

Replacing $V_{\rm p} = V - IR_{\rm s}$, the last relation becomes



Figure 3.5.: Ideal solar cell consisting of a current source $I_{\rm ph}$ shunted by a diode.



Figure 3.6.: Schematic circuit of a real solar cell including an additional shunt resistor $R_{\rm p}$ as well as a series resistor $R_{\rm s}$.

$$I(V) = -I_{\rm ph} + I_{\rm sat} \left(\exp \frac{e(V - IR_{\rm s})}{\xi k_{\rm B} T} - 1 \right) + \frac{V - IR_{\rm s}}{R_{\rm p}}.$$
 (3.9)

The IV curve is substantially modified by these two resistors, since the voltage $V(R_{\rm s}) = IR_{\rm s}$ drops over the serial resistance, whereas the shunt adds the current $I_{\rm p} = V - IR_{\rm s})/R_{\rm p}$ to the output current. The operation mode $V(I = 0) = V_{\rm oc}$ defines the open circuit voltage of a solar cell; $V(I = I_{\rm sc}) = 0$ the short circuit current.

3.7. Photovoltaic parameters

The directly measurable parameters of a photovoltaic cell are the short-circuit current $I_{\rm sc}$, the open circuit voltage $V_{\rm oc}$, the fill factor FF, the power conversion efficiency $\eta_{\rm p}$ and and the incident photon to current efficiency IPCE. In Fig. 3.7 typical IV curves with and without illumination are shown. The dark curve shows a typical diode characteristic. Under illumination the IV curve is shifted towards negative currents because of the photo generated current (see Eq. (3.7)).

• Open circuit voltage $V_{\rm oc}$

The voltage at which no current flows through a solar cell is called open



Figure 3.7.: IV curves with and without illumination of a typical photovoltaic device. $I_{\rm sc}$ is the short-circuit current, $V_{\rm oc}$ is the open circuit voltage, MPP is the maximum power point and $P_{\rm max}$ is the maximum power output of the solar cell.

circuit voltage $V_{\rm oc}$. Several studies have demonstrated a strong dependence of $V_{\rm oc}$ on the energy difference ΔE between the HOMO-LUMO offset at the DA-interface of an organic solar cell (see Fig. 3.8) [40, 41, 42]. However, the experimental values for $V_{\rm oc}$ can differ from those inferred from ΔE for some material systems. This disparity can be the result of special electronic properties of the donor and acceptor at the DA-interface. Thus, a thorough understanding of molecular material properties that influence $V_{\rm oc}$ is important to develop new OPV materials that lead to a high $V_{\rm oc}$ (see chapter 6).

• Short-circuit current $I_{\rm sc}$

For V = 0 only the short-circuit current I_{sc} flows through the solar cell which is purely based on photo generated charge carriers. Thus, for monochromatic exposure the spectral dependence of the charge carrier generation can be measured.

• $\underline{\mathbf{F}}$ ill $\underline{\mathbf{f}}$ actor (FF)

The maximum electric power P_{max} of a photovoltaic cell is determined by the maximum power point in the *IV*-Curve. Therefore, the fill factor is defined as



Figure 3.8.: (a) Layer setup of an organic heterojunction solar cell. (b) Energy level alignment at the DA-interface: The $V_{\rm oc}$ of an organic solar cell is dependent on the energy difference ΔE between the HOMO-LUMO offset of the donor and acceptor material, respectively.

(3.10)

Thus, FF is given by the ratio of gray and red areas in Fig. 3.7. FF is an indicator of the quality of a photovoltaic cell. The fill factor is significantly determined by the serial electrical resistance of the cell and therefore by the mobilities of charge carriers in the organic layers of the cell. Typical values for FF are 0.75 to 0.85 in inorganic solar cells and 0.55 to 0.7 for good organic solar cells.

• <u>Incident-photon-to-current</u> <u>efficiency</u> (IPCE)

The incident-photon-to-current efficiency is defined as the ratio of the number of incident photons $N_{\rm photon}$ and the number of photo induced charge carriers $N_{\rm charge}$ which can be extracted out of the solar cell. It is smaller than the internal quantum efficiency which represents the conversion of absorbed photons into charge carriers within the cell. The reason for this is, that the IPCE takes into account the losses by reflection, scattering and recombination. In contrast to the internal quantum efficiency, which can achieve values up to almost 100 %, the external quantum yield can be directly determined from the short-circuit current $I_{\rm sc}$ and the incident light intensity J_0 [43]:

$$IPCE = \frac{N_{charge}}{N_{photon}} = \frac{I_{sc}}{J_0} \cdot \frac{hc}{\lambda q} , \qquad (3.11)$$

where q is the single electron charge, c is the speed of light, λ is the wavelength of the incident light and h is the Planck constant.

• Power conversion efficiency $\eta_{\rm p}$

The efficiency $\eta_{\rm p}$ is the maximum electrical power $P_{\rm max}$ per light input $P_{\rm L}$.

$$\eta_{\rm p} = \frac{P_{\rm max}}{P_{\rm L}} = \frac{I_{\rm sc}V_{\rm oc}}{J_0} \text{ FF}$$
(3.12)

For an efficient device a large fill factor, a large short-circuit current and a large open circuit voltage is needed. It is not sufficient to optimize only one of these parameters for efficient photovoltaic cells. Since the electrical response of the solar cell on the incident light is strongly dependent on its spectrum, standardized solar simulators which simulate an AM 1.5 spectrum are used for device characterizations.

4. Experimental Methods

In this chapter organic processing technologies which were used during this thesis are reviewed. Furthermore, the basics of ultraviolet and X-ray photoelectron spectroscopy are described. The ultraviolet photoelectron spectroscopy was used to investigate the energetic positions of the Fermi energy $\varepsilon_{\rm F}$ and HOMO levels within a variety of materials during this work. The crystal structure and molecular packing of several organic compounds were explored by X-ray photoelectron spectroscopy.

4.1. Material purification

The purification of organic materials, used in device fabrication, is extremely important to ensure device performance and lifetime [44]. For example, it has been observed that doping anthracene with an impurity content as low as 10^{-7} g/mol (99.99999% purity) significantly reduces the low-temperature hole mobility in crystals [45]. However, this level of purity is still not comparable to Si or other inorganic semiconductors.

Thus, newly synthesized materials have to pass in a first step chemical purifications such as recrystallization, distillation, extraction and adsorption. These purification techniques provide purities up to 99.9% [46, 47]. This level of purity means that in 1000 molecules, on average one impurity molecule will be found, possibly modifying the electrical and optical properties in an undesirable way. Thus, this level of purity is unfortunately insufficient for optoelectronic applications.

In a second step the source materials were therefore further purified by gradient sublimation [44]. Briefly, the material is condensed into a quartz tube under a vacuum of $8 \cdot 10^{-5}$ mbar. Along the length of the tube a temperature gradient is established. The temperature gradient leads to a spacial separation between the compounds. Visual examination of the purification products often allows to decide which product is of the highest purity. In general, the pure product will have a color, texture and/or crystal structure that distinguishes it from the less or more volatile products. The temperature gradient sublimation purification step can vary between values < 10% and over 70%. However, the yield tend to increase for subsequent gradient sublimation cycles as the impurities are separated from the source material. This procedure can be carried out in multiple cycles to achieve the highest possible purity. The limits to the achievable purity are determined by the thermal decomposition of the target compound and the condensation temperature.



b)



Figure 4.1.: (a) Quartz tube connected to the vacuum pump. The physical separation between the compounds can be seen due to the different colors of the materials within the tube. (b) Highly crystalline compound inside of the tube after gradient sublimation.

A picture of recrystallized ZnPc in a quartz tube after gradient sublimation is depicted in Fig. 4.1.

4.2. Device fabrication

The potential advantages of organic electronics compared to conventional semiconductors lie in the production of low-cost, flexible and robust devices filling niches not occupied by Si-based electronics. Therefore, suitable production techniques are needed to deposit and fabricate organic electronic devices. In this section the principles of device fabrication, starting from the substrate design to the material processing by spin-coating and/or thermal vacuum evaporation, are briefly reviewed and explained as these steps are also used here.

4.2.1. The substrate

The prestructured, ITO-covered glass substrates which were used for the fabrication of all electronic devices during this thesis were designed by myself (Fig. 4.2). They were fabricated and delivered by the "Institut für Bildschirmtechnik und Systemtheorie" in Stuttgart. Since highly clean substrates are crucial in terms of device reproducibility and performance, they were produced under clean room conditions and delivered to Ludwigshafen in sealed plastic boxes. Thus, there was no need for an additionally cleaning of the surface by acids and/or liquid solvents. Nevertheless, prior to the fabrication process of organic devices, the substrates were exposed to UV-ozone. This cleaning step removes possible remaining organic adsorbed layers and modify the surface electronic structure.

As shown in Fig. 4.2, 64 devices with 4 different diameters, varying from 0.4 mm to 2 mm, can be fabricated on one substrate. The different diameters were used to investigate the dependence between the active area of the solar cells and the probability of getting shorts. Since it turned out that even the "large" 2 mm devices showed a reliable¹ rectifying behaviour, I changed the substrate design slightly to a 2 mm "only" one. This was done, since a larger active area of the fabricated solar cells lead to higher photo currents which can be measured more precisely without using sophisticated current amplifier. Since always 64 devices were produced per substrate², the experimental results presented in the following chapters are based on the average of at least 64 devices and are therefore highly reliable and meaningful. In App. D an overview of the *IV*-characteristics of 64 $ZnPc/C_{60}$ bulk heterojunction cells evaporated on one substrate is given. During my work I used some hundred substrates and therefore usually even more than one substrate was used per experiment.

¹Usually $\approx 96\%$ of all devices on one substrate worked.

²The tandem cells, presented in Chapt. 8, were produced on FTO-covered glass substrates, since ITO can't withstand the sintering process which was used during the tandem cell fabrication.



Figure 4.2.: (a) Picture of a prestructured ITO-covered glass substrate. As indicated, the active area of the solar cells is defined by a black colored resist. Thus, with the shown substrate one can produce organic solar cells with four different diameters varying from 0.4 mm to 2 mm, respectively. (b) Schematic cross section of the substrate shown in (a). The transparent conducting indium tin oxide (ITO) anode has a sheet resistance of $30 \Omega/cm$.

4.2.2. Spin-coating

Spin-coating is used for the deposition of photoresists and insulating layers in conventional integrated circuit fabrication [48, 49, 50]. Therefore, a small amount of a liquid is dispensed on the substrate which is then accelerated to a spin speed typically in the range 100 rpm to 6000 rpm. During the spinning process, a solid film forms due to the flow and evaporation of the fluid. The thickness of the respective organic layers can be controlled by the spin speed. The dye-sensitized subcell of the novel tandem cell architecture, described later in this work, was fabricated with this technique (see chapter 8.1).

4.2.3. Thermal vacuum deposition

Thermal vacuum deposition is the most commonly used method for depositing low weight organic compounds [44]. The process is based on the sublimation of a compound from a resistively heated boat or crucible in vacuum reaching from 10^{-6} mbar to 10^{-10} mbar onto a substrate [44, 51]. Here, the molecular beam is collimated by the elongate shape of the crucible. The mean free path of the evaporated molecules in the vacuum chamber is usually longer than the size of the chamber. Thus, the molecules could travel from source to the substrate without colliding with molecules inside the chamber. A schematic picture of an evaporation chamber is depicted in Fig. 4.3. The sources are typically located below the substrate to prevent dust and flakes from falling onto the substrate surface. In addition, this arrangement simplifies the use of source materials in granular, powder or liquid form since they are simply held inside the boat or crucible by gravity. The limitation of the evaporation rate is set by the escaperate of the molecules from the solid or molten phase into vacuum, since molecular transport through vacuum is nearly instantaneous. The deposition rate is therefore controlled by the source temperature. Typical rates are 1 Å/s to 10 Å/s, but sometimes also significantly lower as well as higher rates can be used [44]. The use of substrate and source shutters which can rapidly interrupt a molecular beam



Figure 4.3.: Schematic picture of an evaporation chamber. The base pressure within the evaporation tool used for this work varied between $6 \cdot 10^{-6}$ mbar to $2 \cdot 10^{-7}$ mbar.

allow a Å-level control of the evaporated film thicknesses. Quartz crystals are used to monitor the actual deposition rate and film thickness. By thermal vacuum deposition an unlimited number of layers, each optimized for different functions, can be grown in sequence. This feature is an important advantage compared to spin-coating. The flexibility in device design (i.e. materials choice and layer thickness) is an inherent feature of dry processing techniques such as thermal vacuum deposition. Most of the devices described in this work were realized with this fabrication technique. As depicted in Fig. 4.4, the counter electrode of the fabricated solar cells was realized by an evaporated silver layer. While every device had its own ITO-electrode, four cells were sharing one counter electrode. This was possible, since the lateral conductivity of the evaporated organic layers is negligible. A detailed explanation of the device specific fabrication parameters is given directly in the corresponding chapters.

4.2.4. Current-Voltage (IV) measurement setup

A highly precise experimental setup is crucial to ensure a reliable IV-measurement of the fabricated organic solar cells. Additionally, the high amount of devices on each substrate have to be measured in a decent time. Therefore, I established an automized measurement robot in the beginning of my work (see Fig. 4.5). This robot ensures the same horizontal and vertical position of the AM 1.5 light beam in reference to each measured solar cell on the substrate. Furthermore, all cells are measured one after another but within exactly the same time span. Like this, the measurement errors are minimized to the fluctuation of the light spectrum emitted by the AM 1.5 solar simulator.

4.3. Ultraviolet and X-ray photoelectron spectroscopy

Direct photoelectron spectroscopy (PES) is an important general method for mapping out the density of occupied states of a given material. The basic principle of PES is illustrated in Fig. 4.6. When a photon is injected into the sample, it excites an electron from an occupied state to an unoccupied state. If the electron energy is high enough to ionize the respective material, it can escape from the solid into the vacuum and can be detected. Thus, the kinetic energy of the emitted electron can be described by

$$E_{\rm kin} = h\nu - \phi - E_{\rm B} , \qquad (4.1)$$

where E_B is the binding energy of the initial state with respect to the Fermi level, $h\nu$ is the photon energy and ϕ is the work function (Fermi level to vacuum) of the material under study.

Depending on the incident photon energy, different parts of the occupied states are measured. For occupied orbitals which are located 2 eV to 20 eV below



Figure 4.4.: (a) Picture of a prestructured ITO-covered glass substrate. While every solar cell has it's own ITO electrode, the evaporated silver counter electrode is shared by four cells. The sharing of the counter electrode is possible since the lateral conductivity of the evaporated organic layers is negligible. (b) Schematic cross section of the substrate shown in (a) including evaporated organic layers as well as the Ag counter electrode. The area of the organic solar cell is defined by the transparent ITO electrode. The silver counter electrode as well as the ITO electrode are connected to gold contact-pads which can be connected in turn to the measurement system. As indicated, usually the ITO electrode is the anode and the silver counter electrode acts as the cathode.

the Fermi level ε_F , ultraviolet photons (h $\nu \sim 10$ eV to 50 eV) are used. This technique is called ultraviolet photo emission spectroscopy (UPS), and is useful to determine the density of valence states, the work function, and the ionisation potential (IP) of materials [52]. For core levels, X-ray photons (h $\nu > 100$ eV) are used. This technique is called X-ray photo emission spectroscopy (XPS). XPS is

useful in establishing the presence of any element (with the exception of H, and



Figure 4.5.: Picture of the automized IV-measurement robot which I established in the beginning of my work at the BASF. Since the substrate holder can be moved in the *xy*-direction and the light fiber output is movable in the *z*-direction, a precise alignment of all 64 organic solar cells towards the incident light beam is ensured.

He), surface composition, or even depth profile with angle resolved measurement. XPS is one of the most widely used methods to determine the chemical bonding and chemical environment of an element through well established chemical shifts of specific core levels. Typical photon energies for UPS and XPS are shown in Tab. 4.1.

4.4. X-ray scattering

The X-ray scattering technique is a non-destructive analytical technique which can provide information about the crystallographic structure of materials and thin films. X-ray scattering is based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, wavelength or energy. Within this work, two X-ray scattering techniques were used: Singlecrystal X-ray diffraction (XRD) [53] and X-ray powder diffraction (XRPD) [54].

4.4.1. Single-crystal X-ray diffraction (XRD)

Single-crystal X-ray diffraction is a technique to determine the spatial distribution of atoms within a single crystal. During diffraction experiments on single crystals,

source (notation)	Transition Energy (eV)		Relative intensity	
He I He I satellite He II He III	$1s^2 - 1s2p$ $1s^2 - 1s3p$ 1s - 2p 1s - 3p	$21.22 \\ 23.09 \\ 40.48 \\ 48.38$	$ 100 \\ 3-4 \\ 0.1 \\ 0.01 $	
Ne I Ne II	$2p^{6} - 2p^{5}3s$ $2p^{5} - 2p^{4}3s$	$\frac{16.85}{29.6/27.8/30.5}$	$100 \\ 20/10/3$	
Al K α		1486.6		
Mg K α		1283.6		

Table 4.1.: Typical photon lines for UPS and XPS photoelectron spectroscopy. In X-ray spectroscopy, $K\alpha$ emission lines result when an electron transitions to the innermost K shell (principal quantum number 1) from a 2p orbital of the second or L shell (with principal quantum number 2).

a beam of X-rays strikes the crystal and diffracts into many specific directions. From the angles and intensities of these diffracted beams, a three-dimensional picture of the density of electrons within the crystal can be deduced. The mean



Figure 4.6.: Schematic diagram describing the principle of photo emission spectroscopy. A photon of energy $h\nu$ is incident into the sample and excites an electron. With fixed photon energy, the kinetic energy distribution of the excited electron will be the convolution of the filled initial state and the final state. The Fermi energy $\varepsilon_{\rm F}$ of the UPS/XPS measurement setup is usually calibrated with reference to gold since this metal doesn't oxidize. Furthermore, it has to be ensured that the measured UPS/XPS samples are conductive enough to avoid charging effects.

positions of the atoms in the crystal as well as the nature of their chemical bonds can be determined from the measured spatial distribution of the electron density.

4.4.2. X-ray powder diffraction (XRPD)

In contrast to the XRD technique, XRPD is used to characterize the crystallographic structures in polycrystalline or powdered solid samples. X-ray powder diffraction is commonly used to identify unknown substances by comparing the measured diffraction data against the database of the Cambridge Crystallographic Data Center (CCDC)³. If the XRPD technique is used in combination with lattice refinement techniques such as Rietveld refinement [55], it is also possible to deduce structural informations of unknown materials. Powder diffraction is also a common and well known method for determining strains in crystalline materials. An effect of the finite crystallite sizes can be seen as a broadening of the peaks in measured X-ray diffraction patterns. This effect can be explained by the Scherrer equation [56]

$$C = \frac{K\lambda}{\beta\cos\Theta} \,. \tag{4.2}$$

Here C is the mean crystallite dimension, K is the shape factor, λ is the x-ray wavelength, typically 1.54 Å, β is the line broadening at half the maximum intensity (FWHM) in radians, and Θ is the Bragg angle .

³http://www.ccdc.cam.ac.uk

5. Structure-performance relation of metal phthalocyanines in organic heterojunction solar cells

Although metal phthalocyanines (MPc) were one of the first compounds used in organic photovoltaics, twenty years later they are still first choice due to their special physical and chemical properties, investigated by numerous experimental and theoretical studies. Depending on the nature of the central metal atom, MPc based solar cells exhibit markedly different device performance. However, so far it was not clarified on a fundamental level, how the different central atoms influence the optical and electrical behavior of solar cell devices. This chapter offers one possible straightforward explanation for this question. In the following, an experimental and theoretical study on zinc (Zn), copper (Cu), nickel (Ni) and iron (Fe) phthalocyanines is presented in which the fundamental physical origin of their characteristic performance in organic solar cells (Fig. 5.1b) is investigated. The study is restricted to metal-phthalocyanines, having the same molecular structure and symmetry (D_{4h}).

5.1. Device setup and characterization

The organic heterojunction solar cells (HJC's) which I have fabricated for this investigation were evaporated on the prestructured glass substrates shown in Fig. 4.2. As described in chapter 4.2.1, the transparent conducting indium tin oxide (ITO) electrode had a sheet resistance of 30 Ω/cm and an area of 31.5 mm². Prior to organic deposition, I exposed the substrates to UV ozone for 20 min. The organic films and a metal cathode were deposited via high vacuum thermal evaporation under a base pressure of $2 \cdot 10^{-6}$ mbar. I purified the organic source materials by gradient sublimation prior to use. The organic heterojunction solar cells were produced using FePc, NiPc, CuPc and ZnPc respectively as p-conducting and C_{60} as n-conducting organic layers. I evaporated the metal phthalocyanines with rates of 2 Å/s and different layer thicknesses from 10 nm to 60 nm in order to find the optimal layer thickness. This was followed by the layer sequence C_{60} (2 Å/s, 10 nm - 60 nm) and Bphen (0.6 A/s, 6 nm). The cathode was realized by a 100 nm thick silver electrode (5 Å/s) which was evaporated on top of the organic layers (see Fig. 4.4). The structure of the molecules used as well as the device setup are depicted in Fig. 5.1. The open circuit voltage $V_{\rm oc}$, the short circuit current



Figure 5.1.: (a) Chemical structure of the materials used in our bilayer heterojunction solar cell (HJC). (b) Schematic device structure of the HJC.

 $I_{\rm sc}$, the fill factor FF and the power conversion efficiency η were obtained under simulated 100 mW/cm² AM 1.5 white light illumination with the measurement equipment described in chapter 4.2.4. The illumination intensity was adjusted with a calibrated Si detector. Fig. 5.2 shows the I - V characteristics for HJC's with optimized layer layer thicknesses of the MPc's and C₆₀. The respective layer parameters and key characteristics are depicted in Tab. 5.1. With an open circuit voltage $V_{\rm oc}$ of (550 ± 10) mV, a short circuit current $I_{\rm sc}$ of (-5.15 ± 0.2) mA/cm² and an efficiency η of (1.77 ± 0.15) %, ZnPc was identified to be the best performing metal phthalocyanine in our bilayer HJC's. All other MPc's showed reduced device performance in the ordering ZnPc \rightarrow CuPc \rightarrow NiPc \rightarrow FePc.

While the thickness of C_{60} has its optimum at 40 nm for all devices, the optimal layer thickness of the metal phthalocyanines varied from 40 nm for ZnPc to 10 nm for FePc. A complete thickness dependence of I_{sc} is depicted in Fig. 5.2b.

5.2. Thin film characterization

5.2.1. Results of high resolution X-ray powder diffraction (XRPD)

Since I supposed, that the charge transport properties depend sensitively on the thin film structure, I initiated detailed atomic force microscope (AFM) and high



Figure 5.2.: (a) I - V curves of the investigated bilayer heterojunction solar cells: ZnPc/C₆₀, CuPc/C₆₀, NiPc/C₆₀ and FePc/C₆₀. The corresponding device data are given in Tab. 5.1. (b) Thickness dependence of the short circuit current $I_{\rm sc}$ (absolute value) of the MPc/C₆₀ heterojunction devices: The layer thickness of the phthalocyanines was varied from 10 nm to 60 nm, while the C₆₀ layer was kept constant at 40 nm.

MPc	MPc/C_{60} [nm]	$V_{\rm oc}~[{\rm mV}]$	$I_{\rm sc}[{\rm mA/cm^2}]$	$\mathrm{FF}[\%]$	$\eta[\%]$
ZnPc CuPc NiPc FePc	$\begin{array}{c} 40/40 \\ 40/40 \\ 20/40 \\ 10/40 \end{array}$	550 ± 10 520 ± 10 440 ± 10 160 ± 10	$\begin{array}{c} -5.15\pm0.2\\ -4.48\pm0.15\\ -2.67\pm0.09\\ -1.06\pm0.04\end{array}$	63 ± 1 61 ± 1 55 ± 1 42 ± 1	$\begin{array}{c} 1.77 \pm 0.15 \\ 1.42 \pm 0.1 \\ 0.64 \pm 0.05 \\ 0.07 \pm 0.01 \end{array}$

Table 5.1.: Key device characteristics measured for the optimal thickness combination of the MPc and C₆₀ layer. The corresponding I - V curves are shown in Fig. 5.2. The respective measurement errors are caused by small but unavoidable fluctuations of the light intensity emitted by the AM 1.5 solar simulator during the measurement.

resolution x-ray powder defraction (XRPD) measurements. The XRPD experiments were done by Prof. Dr. Robert Dinnebier at the MPI for solid state research and the AFM pictures shown in Fig. 5.4 were recorded by Stefan Schäfer at the BOSCH analytics department. The respective sample preparation as well as the interpretation of the measured data was done by myself.

The high resolution X-ray powder diagrams were recored in order to look for a correlation between device performance and the crystal structure of vacuum deposited ZnPc, CuPc, NiPc and FePc films with thicknesses of 1 μ m and 30 nm (for details see Section A.1). As a result, the XRPD diagram of all investigated materials turned out to be almost identical. For the 1 μ m films seven reflection peaks (Fig. 5.3, Tab. 5.2) were observed. At layer thicknesses of 30 nm only the strongest peak at $2\Theta = 6.8^{\circ}$ could be measured. The peaks at $2\Theta = 21.27^{\circ}$ and 30.17° are attributed to [211] and [222] reflections of the ITO substrate [57]. Comparing the observed reflections with previously published results of MPc films, the crystalline polymorph could be identified as α -phase [58, 59, 60] (Tab. 5.2).

In agreement with present fundamental crystallographic studies [62, 63], the present observations show, that the crystal structure of the investigated MPc films exhibit the α -form [17], e.g. have a triclinic unit cell. Therefore, it became obvious, that the monoclinic β modification [19], having a completely different arrangement shown in Fig. 5.3c, has been erroneously used to describe the crystal packing in previous publications [64, 65, 66].

For the 30 nm vacuum deposited MPc films the calculated crystallite sizes, based on the [010] reflection peak, were found to be identical to the film thickness. For the 1 μ m films no domain sizes > 50 nm were observed in agreement with complementary AFM studies (Fig. 5.4, details in Section A.2): With a diameter of (27.6 \pm 8.7) nm NiPc shows the largest grains followed by ZnPc with (23.6 \pm 8.9)nm, FePc with (22.2 \pm 6.5)nm and CuPc with (21.1 \pm 8.5)nm.



Figure 5.3.: (a-c) Crystal packings of three polymorphic forms of CuPc showing different arrangements of the CuPc molecules: (a) triclinic α -phase [17] showing parallel stacks in a single orientation. (b) Monoclinic β -phase [18] exhibiting a herringbone arrangement and (c) the also monoclinic γ -phase [19] with parallel stacks in a zigzag fashion with a dihedral angle of 54.8° between neighboring stacks. (d) Low angle region of powder patterns of 1 μ m and 30 nm thick, vacuum deposited CuPc films on ITO, compared to calculated powder patterns of α -, β -, and γ -CuPc. (e) Full powder patterns of the 1 μ m and 30 nm thick films shown partly in (d) in logarithmic intensity scale. For the 1 μ m film, a calculated profile is given, consisting of a LeBail fit [61] of the ITO substrate and seven individually fitted peaks of α -CuPc. The peaks markers of the two phases and the difference curve between measured and calculated powder patterns are given below.



Figure 5.4.: AFM images of 30 nm thin films of (b) ZnPc, (c) CuPc, (d) NiP and (e) FePc grown on ITO coated glass. The used ITO (a) is in average very smooth (RMS = 0.48 nm), however slight hight differences of up to 3 nm could be detected (dark parts in the SEM picture).

As no significant differences regarding packing and grain size in the different metal phthalocyanines were found, the performance variation (Tab. 5.1) of the fabricated devices is assigned tentatively to electronic properties.

5.2.2. Absorption and fluorescence of vacuum deposited metal phthalocyanine films

Since no significant structural differences which could explain the characteristic device performance of the MPc's were found, I investigated in a next step the UV-Vis absorption of the MPc films evaporated on quartz glass. As depicted in Fig. 5.5a, the 30 nm thick films showed similar spectra with slight characteristic differences. With respect to the current-thickness dependence shown in Fig. 5.2b it is concluded, that the absorption strength, which varied at most by a factor of two, could not explain the five times higher current of ZnPc compared to FePc in the present solar cells. Thus, the differences in absorption cannot account for the huge differences in the device performance of the MPc's.

The fluorescence spectra of evaporated ZnPc, CuPc, NiPc and FePc films were also measured on quartz glass. The applied technique is explained in Section A.3.

Observed peaks	α -Form [17] P-1	hkl	γ -Form [19] C_2/n	hkl	β -Form [18] $\mathbf{P2}_1/a$	hkl	
6.84	6.82	010	6.73	200	7.04	001	
7.27	7.37	001	7.47	002	-	-	
13.72	13.66	020	13.48	400	14.12	002	
24.00	23.95	10-1	23.90	111	23.85	31 - 2	
25.01	25.00	11-1	24.82	112	-	-	
26.60	26.63	10-2	26.79	312	26.66	11-3	
27.56	27.55	12-1	27.53	31-3	27.65	60-2	

5.3 Ligand-metal exchange coupled states (LMEC states) in metal phthalocyanines

Table 5.2.: Observed reflections of the 1μ m CuPc films in values of 2Θ compared with the calculated powder pattern of α , β , and γ -forms obtained from the Cambridge Crystallographic Data Centre (CCDC). For the 30 nm films only the first reflection at $2\Theta = 6.85^{\circ}$ could be detected.

As depicted in Fig. 5.5b, the fluorescence intensity of ZnPc was measured to be ninety times stronger than that of CuPc. The fluorescence of NiPc and FePc was below the detection limit. Interestingly, in contrast to the very similar structure and absorption characteristics, the fluorescence quantum yield of the investigated MPc films differed tremendously from each other.

5.3. Ligand-metal exchange coupled states (LMEC states) in metal phthalocyanines

To explain the variations of the solid state fluorescence, I initiated further investigations of this effect by quantum mechanical calculations. Therefore I contacted Dr. Jan Schöneboom from the quantum chemistry department of the BASF. He finally did the calculations which are visualized in Tab. 5.3 and Tab. 5.4 as well as in Fig. 5.6, Fig. 5.8 and Fig. 5.7.

The electronic structure of the MPc series (M = Fe, Ni, Cu, Zn) in their ground and excited states can be defined by differential occupations of the representative molecular orbitals (MO's) depicted in Fig. 5.6. Two points have to be emphasised:

- 1. The relevant metal d orbitals are classified according to their representation in D_{4h} symmetry: $b_{2g}(d_{xy})$, $a_{1g}(d_{z^2})$, $1e_g(d_{xz,yz})$, $b_{1g}(d_{x^2-y^2})$.
- 2. The relevant ligand-based molecular orbitals for the low-energy excitations are the a_{1u} orbital (π -orbital) and the set of degenerate $2e_g$ orbitals (π^* -orbitals).



Figure 5.5.: (a) Absorption spectra of 30 nm thick evaporated films of ZnPc, CuPc, NiPc and Fe(II)Pc. (b) Fluorescence spectra of vacuum deposited films of CuPc and ZnPc with a thickness of 800 nm. The films were excited at a wavelength of 532 nm. The fluorescent quantum yield of CuPc is measured to be ninety times weaker than for ZnPc.



Figure 5.6.: Relevant frontier orbitals of the MPc's considered in the present study. Shown orbitals are state-averaged natural orbitals from a DDCI2 calculation [67] on FePc. The corresponding orbitals of ZnPc, NiPc and CuPc are qualitatively the same, with a somewhat larger admixture of ligand π and metal $d_{\rm xz}/d_{\rm yz}$ orbitals.

MPc	State	electronic configuration	CI weight
Fe(II)Pc Ni(II)Pc Cu(II)Pc Zn(II)Pc	${}^{3}A_{2g} \\ {}^{1}A_{1g} \\ {}^{2}B_{1g} \\ {}^{1}A_{1g}$	$\begin{array}{l} (b_{2g})^2, (1e_g)^2, (a_{1g})^2, (a_{1u})^2, (b_{1g})^0, (2e_g)^0 \\ (b_{2g})^2, (1e_g)^4, (a_{1g})^2, (a_{1u})^2, (b_{1g})^0, (2e_g)^0 \\ (b_{2g})^2, (1e_g)^4, (a_{1g})^2, (a_{1u})^2, (b_{1g})^1, (2e_g)^0 \\ (b_{2g})^2, (1e_g)^4, (a_{1g})^2, (a_{1u})^2, (b_{1g})^2, (2e_g)^0 \end{array}$	$0.83 \\ 0.80 \\ 0.79 \\ 0.81$

Table 5.3.: Ground state configurations of the MPc's.

Due to the interaction between the ligand-based molecular orbitals and metal orbitals, so-called ligand-metal exchange coupled states (LMEC states) are formed. Electronic ligand-metal exchange coupling is a general phenomenon observed in many transition metal complexes. An excellent introduction to this subject is given in Ref. [68]. Ligand-metal exchange coupled (LMEC) states which are lower in energy than the optical excited state (i.e. the ligand based $a_{1u} \rightarrow 2e_g$ excitation) were found to be present for all molecules under study but ZnPc. An increasing number of electronically excited states was obtained energetically below the initially excited ligand-based $\pi - \pi^*$ state going from ZnPc (zero) \rightarrow CuPc with one \rightarrow NiPc with two \rightarrow FePc with over six excited states. It is important to note that the LMEC states considered here are of the same spin as the respective

ground states. Therefore, they may be populated on the femto- to picoseconds timescale by internal conversion from the initial ligand excited state (a_{1u}) . This process is expected to lead to a fast depopulation of the initial excited state, and could therefore influence effectively the solid state fluorescence of the corresponding MPc's. In Table 5.3 the ground state configurations of all investigated metal phthalocyanines are summarized, while the excited states are listed in Table 5.4. In the following, the nomenclature for the LMEC states has been adopted from Ref. [68], where ${}^{2S+1}L(M_s){}^{2S'+1}M(M_{s'})$ denotes a LMEC state with a ligand L of multiplicity (2S + 1) and magnetic spin quantum number M_s and a metal M of multiplicity (2S' + 1) and magnetic spin quantum number $M_{s'}$. The nature of the LMEC states are assigned in Table 5.4 accordingly, where appropriate linear combinations are given to account for the correct symmetry of the wave functions. A pictorial representation of the electron population of the leading configurations is given in Fig. 5.8 and Fig. 5.7. Detailed information of the respective calculated excited states of each of the MPc's are presented in the App. A.5.



Figure 5.7.: Electron population of the ground states and lowest excited states shown in Tab. 5.4 for (a) CuPc and (b) ZnPc. The ground state configurations are highlighted green, the states corresponding to the $\pi - \pi^*$ excitation are highlighted red and the LMEC states are highlighted in blue, respectively. Since ZnPc has no LMEC states, only the ligand based $a_{1u} \rightarrow 2e_g$ excitation can take place with an energy of 2.5 eV.



* Triplet state resulting from triplet ligand coupling to triplet metal; corresponding quintet state is shown.





Figure 5.8.: Electron population of the ground states and lowest excited states shown in Tab. 5.4 for (a) FePc and (b) NiPc. For FePc, the configuration $1^{3}B_{2g}$ (d-d excitation) state has been omitted. The ground state configurations are highlighted green, the states corresponding to the $\pi - \pi^{*}$ excitation are highlighted red and the LMEC states are highlighted in blue, respectively.

MPc	State	excitation	energy $[eV]$	nature	CI weight
Fe(II)Pc	$1 \ {}^{3}E_{g}$	$(a_{1g}) \rightarrow (1e_g)$	0.13	metal d-d	0.81
	$1 {}^{3}B_{2g}$	$(a_{1g}, b_{2g}) \rightarrow (1e_g)$	0.69	metal d-d	0.83
	$1 {}^{3}A_{2u}$	$(a_{1u}, a_{1g}) \rightarrow (1e_g, 2e_g)$	0.89	${}^{3}\mathrm{L}(0){}^{3}\mathrm{M}(1) - {}^{3}\mathrm{L}(1){}^{3}\mathrm{M}(0)$	0.63
	$1 {\ }^{3}\mathrm{E_{u}}$	$(a_{1u}) \rightarrow (2e_g)$	1.17	${}^{3}\mathrm{L}(0){}^{3}\mathrm{M}(1) - {}^{3}\mathrm{L}(1){}^{3}\mathrm{M}(0)$	0.77
	$2 {}^{3}A_{2u}$	$(a_{1u}, a_{1g}) \rightarrow (1e_g, 2e_g)$	1.49	${}^{3}\mathrm{L}(1){}^{1}\mathrm{M}(0)$ (tripsinglet)	0.82
	$3 \ ^{3}A_{2u}$	$(a_{1u},a_{1g}) \rightarrow (1e_g,2e_g)$	1.62	$^{1}L(0)^{3}M(1)$ (singtriplet)	0.79
Ni(II)Pc	$1 \ ^{1}E_{u}$	$(a_{1g},a_{1u}) \rightarrow (b_{1g},2e_g)$	2.17	${}^{3}\mathrm{L}(-1){}^{3}\mathrm{M}(1) + {}^{3}\mathrm{L}(1){}^{3}\mathrm{M}(-1) - {}^{3}\mathrm{L}(0){}^{3}\mathrm{M}(0)$	0.83
	$1 \ {}^{1}B_{1g}$	$(a_{1g}) \rightarrow (b_{1g})$	2.50	metal d-d	0.83
	$2 \ ^{1}E_{u}$	$(a_{1u}) \rightarrow (2e_g)$	2.60	ligand $\pi - \pi^*$	0.82
Cu(II)Pc	$1 \ ^{2}E_{u}$	$(a_{1u}) \rightarrow (2e_g)$	1.43	${}^{3}L(0){}^{2}M(1/2) - {}^{3}L(1){}^{2}M(-1/2)$ (tripdoublet)	0.68
	$2 \ ^{2}E_{u}$	$(a_{1u}) \rightarrow (2e_g)$	2.70	ligand $\pi - \pi^*$	0.79
Zn(II)Pc	$1 \ ^{1}\mathrm{E_{u}}$	$(a_{1u}) \rightarrow (2e_g)$	2.50	ligand $\pi - \pi^*$	0.80

Table 5.4.: Calculated lowest excitations of the ground state manifold (SORCI). For explanation of the nomenclature in column "nature" see text.

5.4. Influence of the LMEC-states on the device performance

The similar molecular structure, packing and grain size of the MPc's as well as their absorption offers no explanation for the huge performance variation in organic solar cells. However, the solid state fluorescence spectra of the investigated MPc films were shown to differ significantly from each other. Based on the quantum mechanical calculations of the excited states in the MPc's, there is a strong evidence, that the different fluorescence behaviors are based on characteristic ligand-metal exchange coupled states (LMEC states).

To correlate the influence of the LMEC states with the device performance of the respective phthalocyanines, one has to consider, that excitons diffuse after their generation towards the donor-acceptor interface ¹ with a certain rate $k_{\rm D}$. Concurrently, these excitons could relax non-radiatively with a rate $k_{\rm nr}$ by reducing the excitation energy of the exciton (see Fig. 5.9). In case of the presence of LMEC-states below the $\pi - \pi^*$ excitation $(a_{1\rm u} \rightarrow 2e_{\rm g})$, this relaxation process is supposed to become very likely.

Therefore, it has to be discussed whether the exciton diffusion rate $k_{\rm D}$ or the none radiative relaxation $k_{\rm nr}$ is dominant and therefore responsible for the device performance of the investigated metal phthalocyanines.

5.4.1. Implications on the excitation energy transfer

Incoherent exciton hopping is described in the weak coupling limit, which means that interchromophore electronic coupling is weaker than the donor excited state vibrational reorganisation energy. In this case, the bimolecular rate $k_{\rm D}$ for excitation energy transfer takes the form [69]

$$k_{\rm D} = \frac{2\pi}{\hbar} V_{\rm DA}^2 F_{\rm DA} \tag{5.1}$$

where V_{DA} is the electronic coupling integral for excitation energy transfer and F_{DA} the overlap between donor emission and acceptor absorption spectra, normalized on an energy scale (derived from the Franck-Condon weighted density of states, the product of the density of vibrational states in the initial and final states and their overlap). Under the assumption of separate chromophores, V_{DA} is dominated by the Coulomb integral

$$J = \frac{1}{4\pi\varepsilon_0} \int \vec{dr_1} \vec{dr_2} \phi_{\rm A}^{\rm a_{1u}}(\vec{r_1}) \phi_{\rm A}^{*,2\rm e_g}(\vec{r_1}) \frac{1}{|\vec{r_1} - \vec{r_2}|} \phi_{\rm B}^{\rm a_{1u}}(\vec{r_2}) \phi_{\rm B}^{*,2\rm e_g}(\vec{r_2}) .$$
(5.2)

The wave function $\phi_{\rm A}^{a_{1u}}(\phi_{\rm A}^{*,2e_{\rm g}})$ describes the molecular a_{1u} -orbital ($2e_{\rm g}$ -orbital) on the donor molecule A and $\phi_{\rm B}^{a_{1u}}(\phi_{\rm B}^{*,2e_{\rm g}})$ is the a_{1u} -orbital ($2e_{\rm g}$ -orbital) on the acceptor molecule B. This integral may be approximated by a simple dipole [25, 24]

¹Valid in vacuum deposited organic bilayer and bulk heterojunction solar cells.



Figure 5.9.: (a) Schematic picture describing the influence of the calculated LMEC-state of CuPc (Tab. 5.4) on the exciton transport: CuPc has one additional calculated excitation which is lowered by a ΔE of 1.27 eV compared to the $\pi - \pi^*$ excitation. This intermediate state has the same spin as the respective initial state and therefore may be populated on the femto- to picoseconds timescale by internal conversion. Thus, excitons moving with a rate $k_{\rm D}$ from molecule A to B (the * at A and B in the picture should indicate that the molecules are not charged but excited) towards the donor-acceptor (DA) interface could concurrently relax non-radiative with a rate $k_{\rm nr}$ on molecule B. These relaxed excitons are now trapped as they cannot split at the DA interface due to their reduced excitation energy. Hence, they cannot contribute to the current in an organic solar cell. (b) None radiative energy conversion in a polyatomic molecule is based on the fact, that for each electronic state, there exist a lot of additional vibrational excited states. Therefore, the rate of the none radiative deactivation processes $k_{\rm nr}$ depends on the density $\rho_{\rm v}$ as well as on the overlap of the electronic ϕ and/or vibronic wave functions χ in the final and initial state (Born-Oppenheimer approximation, see Eq. (5.3)).

or even multipole [70, 71, 72] interaction energy. It is noted that a quantitative estimation of intermolecular coupling between closely packed molecules requires also the inclusion exchange and penetration terms [73, 74, 75, 76]. Here, only the excitation energy transfer between the $(a_{1u} \rightarrow 2e_g)$ excited states is considered². Because a_{1u} and $2e_g$ are essentially unaffected by the metal center (depicted in Fig. 5.6), the electronic coupling integral, described in Eq. (5.2), and therefore V_{DA} will be equal for all MPc's.

With respect to the analogy of the absorption and normalized fluorescence spectra (Fig. 5.5), F_{DA} is expected to be similar as well. Based on these perceptions k_{D} can assumed to be similar for all MPc's.

5.4.2. Implications on the non-radiative deactivation

Non-radiative deactivation processes within molecules can be characterized by matrix elements derived from the time-dependent perturbation theory. Under the assumption of weak coupling, the wave functions ψ can be divided in an electronic ϕ and a vibrionic χ part (Born-Oppenheimer approximation). Therefore, the rate for non-radiative deactivation $k_{\rm nr}$ can be written [77] as

$$k_{\rm nr} \sim \frac{2\pi}{\hbar} \langle \phi^f | H' | \phi^i \rangle^2 \langle \chi_i | \chi_f \rangle^2 \rho_v, \qquad (5.3)$$

where H' is the perturbation operator. In the case of internal conversion between states of equal multiplicity (which is the case here) it has been shown, that H' is the operator of the kinetic energy of the cores [77]. Based on Eq. (5.3) it becomes obvious, that the excitation energies (Tab. 5.3) of the respective phthalocyanines must have a significant influence on the radiationless deactivation processes described by k_{nr} : As depicted in Fig. 5.9b the density of states ρ_v in the final state increases with the size of the energy gap ΔE between the final and initial state. At the same time the electronic excitation energy which has to be absorbed by the lattice vibration is also rising. Thus, $\langle \chi_i | \chi_f \rangle^2$ decreases due to the lower overlap of the vibrational wave functions with different vibrational quantum numbers. Concerning the investigated metal phthalocyanines this means, that k_{nr} depends on the number as well as on the energetic difference of the LMEC-states lying in between the initially excited state and the ground state: As more LMEC-states are available and as closer their energetics are, k_{nr} will increase due to Eq. (5.3). Thus, FePc is expected to have the highest relaxation rate k_{nr} and ZnPc the lowest.

²To split excitons at the donor-acceptor interface into free charge carriers it is widely accepted, that the present energetic offset between the HOMO of the donor (metal phthalocyanines) and the LUMO of the acceptor (C₆₀) have to be equal or somewhat larger than the exciton binding energy. Thus, only the $\pi - \pi^*$ excitons are considered to be able to split at the MPc/C₆₀ interface.
5.4.3. Relation to device performance

Exciton transport is in general characterized by the effective exciton diffusion length $L_{\rm ex}$

$$L_{\rm ex} = \sqrt{D \cdot \tau}.\tag{5.4}$$

The lifetime τ is related to $k_{\rm nr}$ as

$$\tau \sim \frac{1}{\sum_{i} k_{i,\mathrm{nr}}},\tag{5.5}$$

while D is directly proportional to $k_{\rm D}$,

$$D \sim k_{\rm D}.$$
 (5.6)

Based on the presented experimental and theoretical results (vide supra) D is assumed to be similar while an increasing number of intermediate states leads to a decreasing τ depending on the metal phthalocyanine of interest. Obviously, the differences in lifetime τ will lead to different values of L_{ex} in the present MPc series. This is in agreement with experimental results [33, 34, 35, 36]. Furthermore, the optimized thickness of the MPc layer in the device decreases in the series ZnPc \rightarrow CuPc \rightarrow NiPc \rightarrow FePc which is another indication that L_{ex} decreases in same series, as less highly excited excitons are able to reach the donor-acceptor interface.

Besides the specific exciton diffusion length $L_{\rm ex}$, I also consider the hole mobility μ to have an influence on $I_{\rm sc}$ and the fill factor. Therefore, the electronic effects which affect the characteristic hole mobility still have to be elucidated; work in this regard is currently on going.

5.5. Conclusion

In summary a study on different metal phthalocyanines (MPc's with M = Zn, Cu, Ni, Fe) was presented in which the fundamental physical origin of their characteristic performance in organic solar cells was investigated under a structural, optical and electronic point of view. MPc/C₆₀ based bilayer heterojunction solar cells exhibited a clear dependence of the optimal layer thickness and overall performance on the employed MPc material. The origin of these differences were explored by AFM and high resolution XRPD measurements on powder and evaporated thin films. In the course of these measurements it was found, that all MPc's exhibit a similar thin film crystal structure. Furthermore, the relation between the known crystal structure of α -CuPc [17] and the molecular packing of vacuum deposited thin films was clarified.

The optical properties of the metal phthalocyanines were investigated by solid state fluorescence and absorption measurements. While the MPc molecules under study had similar absorption characteristics, they differed markedly by their fluorescence spectra. Based on this finding, the lowest excited states of the MPc series were explored by correlated multi-reference ab inito calculations. An increasing number of excited states was obtained energetically below the initially excited ligand-based $\pi - \pi^*$ state going from ZnPc (zero) \rightarrow CuPc with one \rightarrow NiPc with two \rightarrow FePc with over six excited states. These states arise from d-d excitations and ligand-metal exchange coupling. It is argued that an increasing number of intermediate states lead to increasing rates for non-radiative relaxation. This will directly affect the lifetime and therefore the diffusion lengths $L_{\rm ex}$ of photoelectrically active excitons in the present MPc series. Thus, the effect offers a straightforward explanation for the experimentally observed reduced device performances from ZnPc to FePc.

6. The influence of the molecular polarizability on the device performance of organic heterojunction solar cells based on ZnPc and derivatives

The open circuit voltage V_{oc} of small molecule based organic solar cells is usually considerably lower than the HOMO-LUMO offset at the DA-interface of the device which determines the theoretical maximum of the V_{oc} in a first approximation. This is mainly caused by an attractive Coulomb interaction $E_{\rm B} = q^2/4\pi\varepsilon_r\varepsilon_0 r$ between the charge carriers at the interface. It has to be mentioned, that the charge carriers in organic semiconductors are rather polarons and holons than electrons and holes (see chapter 2.3 and 3.2). Since the LUMO (HOMO) is defined to be the electron affinity (ionization potential) of initially uncharged molecules, these energies do not exactly describe the energy levels of polarons and/or holons, respectively (see Fig. 3.2). However, it is very difficult to evaluate exact values for the energetical relaxation of a polaron (holon) in organic semiconductors. Therefore, it is widely accepted to use the HOMO-LUMO offset at the DA-interface of the device in a first approximation to estimate the open circuit voltage of organic solar cell to

$$eV_{\rm oc} \approx |LUMO_{\rm A}| - |HOMO_{\rm D}| - \frac{q^2}{4\pi\varepsilon_r\varepsilon_0 r}$$
 (6.1)

Here, ε_0 represents the vacuum permittivity, ε_r is the relative dielectric constant of the organic material, and r is the initial separation distance of the optically generated charge carrier pair at the DA interface. Furthermore, HOMO_D is the highest occupied molecular orbital of the donor, LUMO_A the lowest unoccupied molecular orbital of the acceptor. As shown in Eq. (6.1), $E_{\rm B}$ is determined by the relative dielectric constant of an organic material which is microscopically related to the molecular polarizability α .

In the following, the influence of the interplay between molecular ordering and polarization effects at the DA-interface on the open circuit voltage $V_{\rm oc}$ of organic heterojunction solar cells (HJC) is investigated. Therefore, novel zinc phthalocyanine (ZnPc) derivatives were synthesized having phenyl, naphthyl or anthracenyl



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Figure 6.1.: a) Chemical structure of the materials used in the bilayer heterojunction solar cell (HJC). The respective ionization potentials (IP) were obtained from UPS measurements (Fig. 6.5). (b) Schematic device structure of the HJC.

groups attached to basic ZnPc cores. The idea behind attaching bulky groups with increasing size to basic ZnPc cores was the successive increase of the molecular polarizability of the respective molecules. The ZnPc derivatives were synthesized by Dr. Sudhakar Sundarraj (BASF South East Asia) according to my structural specifications.

In the following, a promising approach way will be presented, describing a way how to reduce the loss of V_{oc} in organic solar cells.

6.1. Device setup and characterisation

The organic heterojunction solar cells (HJC's) which I have fabricated for this investigation were evaporated on the prestructured glass substrates shown in Fig. 4.2. As described in chapter 4.2.1, the transparent conducting indium tin oxide (ITO) electrode had a sheet resistance of 30 Ω /cm and an area of 31.5 mm². Prior to organic deposition, I exposed the substrates to UV ozone for 20 min. The organic films and a metal cathode were deposited via high vacuum thermal evaporation under a base pressure of $2 \cdot 10^{-6}$ mbar. I purified the organic source materials by gradient sublimation prior to use. The heterojunction solar cells (HJC) were produced containing respectively ZnPc and the novel synthesized Ph-ZnPc, N-ZnPc and A-ZnPc as donors and C₆₀ as electron accepting organic layers. I evaporated the zinc phthalocyanine derivatives with rates of 2 Å/s and



Figure 6.2.: a) I - V curves of the investigated bilayer heterojunction solar cells: ZnPc/C₆₀ (black), Ph-ZnPc/C₆₀ (red) and N-ZnPc/C₆₀ (green). b) Due to the drastically decreased device performance of A-ZnPc/C₆₀ (blue) compared to the other ZnPc derivatives, the I - V characteristic is depicted here separately. The corresponding device data of the ZnPc, Ph-ZnPc, N-ZnPc and A-ZnPc based solar cells are given in Tab. 6.1.

Donor	$\mathrm{Donor}/\mathrm{C}_{60}~\mathrm{[nm]}$	$\eta [\%]$	$V_{\rm oc} [{\rm mV}]$	$I_{\rm sc}[{\rm mA/cm^2}]$	$\mathrm{FF}[\%]$
ZnPc Ph-ZnPc N-ZnPc A-ZnPc	40/40 20/40 10/40 10/40	$\begin{array}{c} 1.77 \pm 0.2 \\ 1.82 \pm 0.1 \\ 1.48 \pm 0.1 \\ 5 \cdot 10^{-3} \pm 2 \cdot 10^{-3} \end{array}$	550 ± 10 680 ± 10 760 ± 10 790 ± 10	$\begin{array}{c} -5.15\pm0.2\\ -4.19\pm0.15\\ -3.24\pm0.11\\ -0.03\pm0.01\end{array}$	63 ± 1 64 ± 1 60 ± 1 22 ± 1

Table 6.1.: Device data measured for the optimal layer thickness combination of the ZnPc derivative donors and C_{60} acceptors. The corresponding I-V curves are shown in Fig. 6.2. The respective measurement errors are caused by small but unavoidable fluctuations of the light intensity emitted by the AM 1.5 solar simulator during the measurement.

layer thicknesses of 10 nm to 60 nm. This was followed by a C_{60} layer (2 Å/s, 10 nm - 60 nm) and a 6 nm thick Bphen (4,7-diphenyl-1,10-phenanthroline) layer (0.6 A/s). The cathode was realized by a 100 nm thick silver electrode (5 A/s) which was evaporated on top of the organic layers (see Fig. 4.4). A schematic picture of the layer setup, as well as the structure and the ionization potential (IP) of the donor molecules, are depicted in Fig. 6.1. The open circuit voltage $V_{\rm oc}$, the short circuit current $I_{\rm sc}$, the fill factor FF and the power conversion efficiency η were obtained under simulated 100 mW/cm² AM 1.5 white light illumination with the measurement equipment described in chapter 4.2.4. The illumination intensity was adjusted with a calibrated Si detector. Fig. 6.2 shows the I - Vcharacteristics for ZnPc (derivatives)/ C_{60} HJCs with optimized layer thicknesses. As depicted, the voltage increased from 550 mV to 790 mV by adding phenyl, naphthyl and anthracenyl groups respectively to a ZnPc core molecule. While the current decreases slowly from ZnPc to N-ZnPc with a coincidental high fill factor around $(62\pm1)\%$, a drastic drop of these parameters was observed from N-ZnPc to A-ZnPc. Within the investigated molecules Ph-ZnPc provided the best ratio between current, voltage and fill factor resulting in the highest power conversion efficiency of $\eta = (1.82 \pm 0.1)\%$.

6.2. Structural analysis

The influence of polarization effects on the device performance is considered to depend strongly on the structural arrangement of the molecules. Thus, I have initiated single crystal XRD, XRPD and UV-Vis absorption investigations of the molecular packing of the different ZnPc derivatives. While I did the UV-Vis absorption experiments, Dr. Wolfang Höffken and Antti Ojala (BASF analytics department) analyzed the respective compounds by synchrotron XRD at the beamline PX III at the SLS in Basel. The long range ordering of the ZnPc-derivatives were investigated by XRPD at 30 nm thick films, which I have evaporated on quartz glass. The XRPD spectra of these films which are shown in App. B were measured by Mr. Ojala (PhD student at BASF) in the analytics department in Ludwigshafen.

Due to the sparing solubility of the pigments, thermal evaporation technique was used to grow crystals of Ph-ZnPc and N-ZnPc for single crystal XRD analysis (see Tab. 6.2 and App. B). For A-ZnPc no suitable single crystals were obtained as it condensed only as a fine semi-crystalline powder. For ZnPc, I have taken already published crystallographic data from existing literature [58, 62, 63, 59].

The crystal structure of α -ZnPc stack in parallel columns in a triclinic crystal system [58, 62, 63, 59]. The translational offset of 1.58 Å leads to a 75° slip angle. The intermolecular distance of the adjacent π -systems stack with a van der Waals distance of 3.42 Å(see Figs. 6.3a and b).

Interestingly, a similar stacking was observed for Ph-ZnPc despite the presence of its phenyl side groups (see Figs. 6.3c and d). The two phenyl groups at the ortho positions are observed to be distorted by angles of 52° and 35°, respectively. Therefore, the π -systems of the adjacent ZnPc core units could stack tightly with a distance of 3.26 Å. The molecules crystallize in P-1 space group and stack in parallel columns along the a axis. Within the columns, the molecules have a translational offset of 1.99 Å and a slip angle of 59° which tilt the stacking direction by 31° in relation to the normal of the molecular plane.

In contrast to ZnPc and Ph-ZnPc, N-ZnPc provides a completely different struc-

	Ph-ZnPc	N-ZnPc
Q	D 1	τ
Space group	P-1	$14_1/a$
Z	1	8
a	3.8200(8)	26.034(4)
b	15.330(3)	26.034(4)
с	16.950(3)	15.240(3)
α	66.99(3)	90
eta	89.45(3)	90
γ	87.16(3)	90
Cell V $[A^3]$	912.5	10329.3
$\rho ~[{\rm g/cm^3}]$	1.606	1.392
R1, Rw	0.045, 0.12	0.095,0.24

Table 6.2.: Crystallographic key parameters of Ph-ZnPc and N-ZnPc measured by the BASF analytics department by synchrotron XRD at the beamline PX III at the SLS in Basel. For more detailed information see App. B.



Figure 6.3.: Crystal structure of ZnPC, Ph-ZnPc and N-ZnPc. (a) The packing of the α -ZnPc on the b-c plane and (b) along the a axis. (c) The packing of the Ph-ZnPc on the b-c plane and (d) along the a axis. (e) The packing of N-ZnPc viewed on the a-b plane. (f) is showing the dimer of N-ZnPc. Hydrogen atoms are omitted in (e).

ture. The molecules were observed to crystallize in tetragonal crystal systems within the space group I4₁/a (see Fig. 6.3c and d). The bulky naphthyl side groups are located at the ortho position. Thus, they point nearly orthogonal to the phthalocyanine plane and prevent the adjacent conjugated π -systems stack in a parallel arrangement. Instead of the columnar structure, the neighboring chro-



Figure 6.4.: UV-Vis absorption spectra of 30 nm thick evaporated ZnPc, Ph-ZnPc, N-ZnPc and A-ZnPc films on quartz glass.

mophores stack perpendicular to each other by the tilted naphthyl groups. The bulky groups were measured to lie parallel to the adjacent phthalocyanine core unit plane within a van der Waals distance of 3.36 Å (Figs. 6.3e and f).

Complementary to the single crystal analysis, the long range ordering of the ZnPc-derivatives were investigated by XRPD at 30 nm thick films, which I have evaporated on quartz glass. It was observed, that only ZnPc films are highly (poly) crystalline. Ph-ZnPc showed a weak peak around $2\Theta = 5^{\circ}$ indicating a very low degree of long range ordering (For more detailed information see App. B). Furthermore, the N- and A-ZnPc films did not show any long range ordering. The XRPD studies are supported by the absorption spectra of the 30 nm thick films of the respective materials depicted in Fig. 6.4. Strong interaction between the adjacent π -system in the ZnPc films give rise to the broadest spectrum whereas the line width of the peaks gets narrower in the successive order of the growing steric bulkiness of the side groups. This effect is attributed to the weaker or fully prohibited interaction of the π -systems on the substituted ZnPc's. This is best pronounced for A-ZnPc, which provides similar thin film and solution spectra showing merely isolated chromophores.

6.3. Polarizability of the ZnPc derivatives

The static molecular polarizability of the molecules under study was calculated by quantum mechanical methods, in particular by time-dependent density functional theory. These calculations were initiated by me and performed by Dr. Jan Schöneboom (BASF computational department). After initial geometry optimization, the molecules were oriented such that the phthalocyanine moiety lies within the xy plane. Due to symmetry, the principal components of the polarizability tensor α_{xx} and α_{yy} are equal and distinct from the α_{zz} component. The results for these components as well as the isotropic polarizability, i.e., $1/3 \operatorname{trace}(\alpha)$, are listened in Tab. 6.3. As expected, the molecular polarizability increases with the attachment of increasingly large substituents in the order (none) \rightarrow phenyl \rightarrow naphthyl \rightarrow anthracenyl. In the same series the molecules become more and more isotropic, as the ratio between $\alpha_{xx,uy}$ and α_{zz} decreases. Comparing the isotropic polarizabilities, there is a two-fold increase in going from ZnPc to the largest derivative, A-ZnPc. An indirect experimental proof for an increased α from ZnPc \rightarrow Ph-ZnPc \rightarrow N-ZnPc \rightarrow A-ZnPc was adduced from UPS measurements¹ as depicted in Fig. 6.5: Similar IP levels of (5.2 ± 0.1) eV for all ZnPc-derivatives suggest an equal dielectric constant ε_r of the materials at the surface. For an isotropic material the relation between α and $\varepsilon_{\rm r}$ is expressed by the Clausius-Mossotti equation

$$\frac{(\varepsilon_r - 1)M}{(\varepsilon_r + 2)\rho} = \frac{N\alpha}{3\varepsilon_0},\tag{6.2}$$

where M is the molecular mass, ρ the density and N the Avogadro constant. Since the ratio M/ρ between the molecular mass M and the density ρ increase from ZnPc to A-ZnPc, Eq. (6.2) suggests strongly, that also the polarizability α has to increase in the same direction in order to provide equal dielectric constants. A similar balance between the molecular polarizability α , molecular mass M and density ρ at the surface of evaporated films has been already shown for a number of polycyclic aromatic hydrocarbons [78].

¹The preparation of the samples as well as the analysis and interpretation of the UPS spectra were done by myself. The UPS spectra itself were measured by Dr. Sabine Hirth (BASF analytics department)



Figure 6.5.: Measured UPS spectra (He I, 21.22 eV) of 30 nm thick evaporated ZnPc, Ph-ZnPc, N-ZnPc and A-ZnPc layers.

Molecule	$\alpha_{xx,yy}$ [au]	α_{zz} [au]	$1/3$ trace (α) [au]	$V_{\rm oc}~[{\rm mV}]$	Density $[g/cm^3]$	Mass $[g/mol]$	Molecules per unit cell
ZnPc	874	151	633	550 ± 10	1.62	577.91	1
Ph-ZnPc	1259	345	954	680 ± 10	1.61	882.3	1
N-ZnPc	1298	693	1096	760 ± 10	1.39	1082.55	8
A-ZnPc	1417	1143	1325	790 ± 10	-	1297.82	-

Table 6.3.: TD-DFT calculated static polarizability (in atomic units [au]). The values for the density, and molecules per unit cell are based on the respective crystal structures. Since no crystallinity could be observed for A-ZnPc, the respective data is missing.

6.4. Discussion of charge separation at the $C_{60}/ZnPc$ (derivative) interface

It has been reported, that usually no interface dipoles are present at organicorganic interfaces if both materials are undoped [79, 80], including CuPc-C₆₀ interface [81].

Therefore, it is assumed that also ZnPc and its derivatives form interfaces governed by vacuum level alignment with C_{60} . Thus, the HOMO_D and LUMO_A offset is simply given by IP(donor) - EA(acceptor). As discussed, similar IP for ZnPc and the respective derivatives were observed by UPS. This suggests strongly, that the increase in V_{oc} from 550 mV to 790 mV by using the highly polarizable A-ZnPc instead of ZnPc, depends mainly on different Coulomb binding energies of



Figure 6.6.: Molecular arrangements used for the charge separation simulation at the C_{60} /Ph-ZnPc (a) and C_{60} /N-ZnPc (b) interface. Picture (a) and (b) show the 1-4 chain configuration. The arrangements of the ph-thalocyanine derivatives were obtained from XRD single crystal analysis.

charge carriers at the DA-interface (Eq. (6.1)). To estimate the energetic influence of polarization effects, I have initiated quantum mechanical calculations of the charge separation mechanism. To built up model systems for this theoretical investigation, I have chosen Ph-ZnPc and N-ZnPc due to their completely different single crystal structures: As depicted in Fig. 6.6, the first donor molecule were placed in an edge-on geometry relative to C_{60} in order to model the maximum polarization effect. The positions of the following donor molecules were taken from the corresponding measured crystal structures (*vide supra*). Finally two different molecular chains of a total length of five molecules were formed (see Fig. 6.6). Based on these model systems, Dr. Christian Lennartz (BASF computational department) did the quantum mechanical evaluation of the electrostatic interaction $E_{\rm B}$ of the charge carrier pair with respect of their distance on the chain.

The electrostatic interaction $E_{\rm B}$ of the charge carrier pair was calculated classically via Coulombs law where atom centered charges were use derived from DFT calculations. Furthermore, the same point charge sets were subsequently used to quantum mechanically polarize the electron cloud of the remaining neutral molecules of the respective chain. The sum of the classical Coulomb interaction energies $E_{\rm B}$ and the quantum mechanically calculated polarization energies $E_{\rm pol}$ sum up to the total electrostatic energy $E_{\rm s}$ of the specific chain configuration. By

Molecule	d [Å]	\mathbf{Po} $E_{\mathrm{B}} [\mathrm{eV}]$	s. 1-2 E _{pol} [eV]	$E_{\rm s} \; [{\rm eV}]$	d [Å]	$\begin{array}{c} \mathbf{Po}\\ E_{\mathrm{B}} \ [\mathrm{eV}] \end{array}$	s. 1-3 E _{pol} [eV]	$E_{\rm s} \; [{\rm eV}]$
Ph-ZnPc	$14.20 \\ 14.14$	-1	0	-1	30.78	-0.38	-0.20	-0.58
N-ZnPc		-1	0	-1	24.03	-0.57	-0.27	-0.84

Molecule	$\begin{array}{c c} \mathbf{Pos. 1-4} \\ d \ [\text{\AA}] & E_{\text{B}} \ [\text{eV}] & E_{\text{pol}} \ [\text{eV}] & E_{\text{s}} \ [\text{eV}] \end{array}$			$\begin{array}{ c c c c c c c c c c c c c c c c c c c$				
Ph-ZnPc	47.64	-0.21	-0.18	-0.39	64.50	-0.12	-0.17	-0.29
N-ZnPc	33.96	-0.42	-0.31	-0.73	43.91	-0.31	-0.26	-0.57

Table 6.4.: Calculated classical Coulomb interaction energies $E_{\rm B}$, polarization energies $E_{\rm pol}$ and the total electrostatic energy $E_{\rm s}$ of the specific chain configuration at a defined distances d. A graphical distribution of $E_{\rm B}$ and $E_{\rm s}$ is depicted in Fig. 6.7.

repeating these calculations for all hopping steps, the potential energy surface of the charge migration process could be analyzed (Fig. 6.7). The values for $E_{\rm B}$, $E_{\rm pol}$ and $E_{\rm s}$ with respect to the distance of the charges are depicted in Tab. 6.4.

It can be observed, that the alternating packing motive (edge on, side on, edge on) of N-ZnPc lead to much stronger polarization effects at the C_{60} /N-ZnPc interface than at the C_{60} /Ph-ZnPc interface. Thus, a suitable preferred orientation



Figure 6.7.: Distribution of the classical Coulomb interaction energies $E_{\rm B}$ in comparison to the total electrostatic energy $E_{\rm s}$, including polarization effects of the specific chain configurations of (a) Ph-ZnPc and (b) N-ZnPc.

of molecules [82, 83] in close distance to the $C_{60}/ZnPc$ (derivative) interface could lead to considerably different Coulomb interactions of the respective charges. As depicted in Fig. 6.7, this results into a significantly higher energetic difference of E_B and E_s leading to a more shallow increase of E_s with increasing distance to the DA-interface for the N-ZnPc setup than for the Ph-ZnPc system. Thus, less energy is required to separate the charges from the DA-interface due to a smaller Coulomb interaction within N-ZnPc. According to Eq. (6.1) these different Coulomb interactions offer a straightforward explanation for the experimentally observed increased open circuit voltage from Ph-ZnPc to N-ZnPc.

Although my model systems were restricted to only five molecules due to the high computational effort, the calculations indicate, that $E_{\rm s}$ will saturate at material specific values $E_{\rm s} < 0$ with increasing distance to the DA-interface. Thus, $E_{\rm s}$ becomes mainly dependent on the interaction between the point charges and the polarized neutral surrounding molecules rather than on the direct Coulomb interaction of the charge carrier carrier pair with increasing distance to the DA-interface. The experimentally shown increase of α and $V_{\rm oc}$ in the order ZnPc \rightarrow Ph-ZnPc \rightarrow N-ZnPc \rightarrow A-ZnPc (Tab. 6.3) together with the calculations on the Ph-ZnPc and N-ZnPc model systems (*vide supra*) indicate, that the different observed open circuit voltages within the whole ZnPc-derivative series are based on different Coulomb interactions induced by characteristic polarization effects of the respective molecules at the DA-interface.

6.5. Conclusion

Heterojunction solar cells were produced containing respectively ZnPc, Ph-ZnPc, N-ZnPc and A-ZnPc as p-conducting and C_{60} as n-conducting organic layers. By adding defined bulky groups to the ZnPc core, the polarizability α of the molecules was successively increased. Concurrently an increase in $V_{\rm oc}$ from 550 mV to 790 mV by using the highly polarizable A-ZnPc instead of ZnPc was observed. Quantum mechanical calculations, simulating the charge separation mechanism at the DA-interface of Ph-ZnPc and N-ZnPc showed, that the interplay between characteristic packing and polarization effects could lead to considerably different Coulomb interactions of the electron-hole pair at the DA-interface. Thus, the discussed experimental and theoretical observations strongly imply, that the increase of $V_{\rm oc}$ in the fabricated heterojunction solar cells in the order $\rm ZnPc \rightarrow Ph-ZnPc \rightarrow$ $N-ZnPc \rightarrow A-ZnPc$ is mainly based on different Coulomb interactions induced by characteristic polarization effects of the respective molecules at the DA-interface. Hence, in contrast to similar dielectric constants ε_r measured by UPS on the surface of the respective 30 nm thick samples (vide supra), ε_r is considered to vary for the different materials right at the DA-interface due to a characteristic interface induced packing. Based on the discussed findings, a high molecular polarizability might be one important property for the design of active materials for high efficient organic solar cells. It is worthwhile to mention, that polarization effects as described in this chapter are not of importance in inorganic semiconductors due to their high dielectric constant (see Tab. 2.1).

7. A novel p-dopant with low diffusion tendency and its application to organic light-emitting diodes

In this chapter the influence of the molecular weight and structure on the diffusivity of organic p-dopants will be investigated. Therefore, a novel p-dopant 2,3-di(N-phthalimido)-5,6-dicyano-1,4-benzoquinone (BAPD, Fig. 7.3a) was developed and compared to the state-of-the-art p-dopant F_4TCNQ (for synthesis details see App. C). The idea for the chemical structure of the novel p-dopant was born in the course of the "Organic-Dopants" research project inside BASF: During this project, I was doing the device tests of the organic dopants which were synthesized by the chemists. With my feedbacks, ideas and proposals¹ I was contributing to the success of this project which finally lead to the synthesis of BAPD. The synthesis was done by Dr. Jianqiang Qu (BASF research department). I investigated the device properties of the organic p-dopants with help of α -NPD/Alq₃-based OLED devices instead of solar cells. The reason for this is based on a technical issue: Most organic dopants are very small and tend therefore to diffuse [79, 84, 85]. This diffusion makes it difficult to fabricate interface-only doped devices [79, 86] because dopants tend to penetrate into other layers of the device and thereby change their composition and electrical properties. In contrast to phthalocyanines which have usually a crystalline layer structure, α -NPD transport layers which are used in standard OLED devices are amorphous. This amorphous structure can suppress the diffusion process partly such that the electronic influence of the p-dopants on the device can be investigated.

After a brief general introduction about OLED's, the device performance of BAPD is compared to F_4 TCNQ. Following, the experimental results concerning the diffusion characteristics of the p-dopants will be presented and discussed.

¹E.g. the increase of the molecular weight and bulkiness of organic dopants in order to achieve a higher thermal stability as well as a reduced diffusivity of the dopants within the evaporated layers.

7.1. Working principle of an organic light emitting diode (OLED)

Tang et al. demonstrated highly efficient organic light-emitting diodes (OLEDs) first in 1987 [87]. Nowadays, such applications are already commercial on small scales. Organic light-emitting diodes (OLEDs) are expected to become the next-generation flat-panel displays and solid state lighting devices because of their low power consumption, high brightness, high contrast and low costs [3, 88, 89, 90, 91].

Fig. 7.1 shows the cross section of a standard multilayer OLED setup. It consists of two organic layers between two electrodes, the anode and the cathode. The typical thickness of the organic layers is less than 100 nm. The entire structure is fabricated on a substrate, which may consist of glass or a flexible polymer film, or even of a silicon wafer. For an efficient light extraction out of the device, at least one of the two electrodes has to be transparent. Often, the extraction is carried out through the anode which usually consists of indium tin oxide (ITO), which is electrically conductive and transparent. The operating principles of an OLED (see Fig. 7.1) are similar to inorganic LEDs. These are

- 1. injection of electron and holes into the device,
- 2. transport of the charge carriers,
- 3. exciton formation,
- 4. recombination of the excitons under emission of light.

The respective organic layers within an OLED are characterized by their HOMO and LUMO energy levels. Thus, the energy gap, the binding energy of the excitons and hence the wavelength of the emitted light are material dependent. Due to the wide variety of usable organic semiconductors it is possible to produce OLED's for nearly the entire visible spectral range. The anode of an OLED usually consists of a metal having a high work function Φ_a from which holes can be injected in the HOMO of the organic layer. As depicted in Fig. 7.1, an activation barrier $\Phi_{B,h}$ must be overcome. The cathode consists of a metal having a low work function $\Phi_{\rm c}$. Thus, electrons can be injected to the LUMO by overcoming the activation barrier $\Phi_{B,e}$. The two different electrodes are connected by the organic layers in between, leading to an electric built-in field. This field prevents the transport of injected charge carriers, if no external field is applied. An overcompensation of the built-in field by an externally applied voltage lead to a current flow through This case is shown in Fig. 7.1c. When electrons and holes meet the device. each other, they could form singlet or triplet excitons. The recombination of singlet excitons results into fluorescence, the recombination of triplet excitons into phosphorescence, respectively. Any non-radiative recombination reduces the light output of OLEDs. A typical value for the HOMO-LUMO gap in an OLED is $\approx 3 \text{ eV}$. Typical driving voltages of an organic light emitting diode lie in between 3 V and 6 V.

The luminous efficiency η_0 of an OLED characterizes the external light output. It is defined as the ratio of the emitted light M_1 (spectral integral) and the injected electrical power [93]:



Figure 7.1.: Operational principle of a two-layer OLED: (a) HOMO-LUMO energy levels of two organic semiconductors which are neither connected with each other nor in contacted with the two metal electrodes, which differ in their work function Φ_a and Φ_c . A typical material for an electron transport layer (ETL) is Alq₃. For the hole transport layer (HTL) amorphous α -NPD is often used. (b) All layers shown in (a) are connected. Due to the Fermi level alignment of all materials, an internal electric field is present which causes a gradient of the respective HOMO and LUMO levels of the organic semiconductors within the device. (c) The device is biased in the forward direction. Thus, the energies E(x) of the HOMO's and LUMO's are functions of the sum of the built-in field and an externally applied electric field. If the external field is strong enough, charge carries can be injected which may form Frenkel excitons at the interface and finally recombine under light emission.



Figure 7.2.: Schematic overview describing the influence of a doped organic layer on the energetic alignment at the metal-organic interface: To run an OLED, holes have to be injected from a metal anode in the HOMO of an organic hole transport layer (HTL). Therefore, the carriers have to overcome an activation barrier $\Phi_{B,h}$. This happens mainly by tunneling. To increase probability of the tunneling process, the width d_t of the tunnel barrier can be reduced by p-doing the hole transport layer [21, 92]. This leads to a decrease of the driving voltage of an OLED [27]. (a) is showing the undoped case where the intrinsic organic layer lead to a broad tunnel barrier. The highly p-doped HTL shown in (b) lead to considerably smaller tunnel barrier due to a stronger band bending of the doped HTL.

$$\eta_{\rm o} = \frac{M_{\rm l}}{IV} \tag{7.1}$$

By doping the hole transport layer, the Fermi level $\varepsilon_{\rm F}$ of the metal anode and the organic semiconductors can be aligned energetically in a more favorable way, leading to a decrease width $d_{\rm t}$ of the tunnel barrier [27] (see Fig. 7.2). This results into a decrease of the driving voltage of an OLED [27] and therefore to a higher luminous efficiency $\eta_{\rm o}$ of the device.

7.2. OLED fabrication

The hole injection layers (HIL) which I have fabricated were made of F_4 TCNQ or BADP doped into N,N-diphenyl-N.N'-bis(1-naphthyl)-1,1-biphenyl-4,4-diamine

(α -NPD). They were vacuum co-evaporated on indium tin oxide (ITO) substrates (Fig. 4.2) with a sheet resistance of 30 Ω /cm. On top of the HIL, organic layers were vacuum deposited at a base pressure of $1 \cdot 10^{-7}$ mbar. α -NPD was deposited as the hole transport layer (HTL), and aluminum tris(8-hydroxyquinoline) (Alq₃) was deposited as an electron-transporting emitting layer. Finally, LiF and aluminum were vacuum-deposited using a metal shadow mask to define an emitting area of 4.0 mm². The device structure is depicted in Fig. 7.3. After the cathode formation, the devices were encapsulated using UV-epoxy resin and a glass lid with an attached desiccant bag under a dry nitrogen atmosphere (<1:0 ppm H₂O and O₂). Luminance and operational lifetime measurements were carried out at room temperature.



Figure 7.3.: (a) Chemical structure of the emitter Alq₃, p-dopants F_4TCNQ and BAPD with electron affinity EA [94], HTL α -NPD with ionization potential IP. The quantum mechanical calculations concerning the electron affinity and ionization potentials were done by Dr. Imke B. Müller (BASF quantum-chemistry department). (b) Schematic OLED device setup.

7.3. Thermal stability and evaporation temperature of the investigated organic dopants

Due to the high molecular weight, BAPD evaporates at $(150 \pm 10)^{\circ}$ C under a vacuum of 10^{-7} mbar. As a comparison, F₄TCNQ evaporates at $(90 \pm 10)^{\circ}$ C at the same pressure. Since the thermal stability of the dopants is important for the processability, I have sent both dopants to the analytics department within the BASF where a thermogravimetric analysis (TGAs) of both compounds were made. Here, BAPD shows a higher thermal stability ($(1 \pm 0.4)\%$ weight loss at 403°C) than F₄TCNQ ($(1 \pm 0.4)\%$ weight loss at 268°C).

7.4. OLED results

In order to investigate the potential of the new dopant, standard OLED devices [95] with a 2 weight% (wt%) p-doped α -NPD hole injection layer (HIL) and an Alq_3 emitter (Fig. 7.3b) were prepared on the substrates shown in Fig. 4.2. The BAPD-doped device showed a slightly higher turn-on voltage (Fig. 7.4a), which is in agreement to the expected less efficient host-to-dopant electron transfer from α -NPD to BAPD compared to F₄TCNQ: The UPS investigation which will be presented in the following chapter, as well as the energatical distance of the calculated electron affinity of BAPD and F₄TCNQ compared to the ionization potential of the host material Alq₃ (see Fig. 7.3a) strongly suggests, that F_4TCNQ will be the more efficient dopant. The current efficiency of the BAPD-doped device was slightly higher than the F_4TCNQ -doped device (3.6 cd/A and 2.6 cd/A at 500 cd/m^2 , respectively), which could be due to a better balance of the amount of holes and electrons recombining at the DA-interface within the diode: Ideally exactly the same amount of electrons and holes should reach the interface in order to convert all their potential energy into light. An asymetric charge carrier transportation leads to the fact, that less energy is converted into light but into phonons which can destroy molecules and finally leads to a fast degradation of the device. The diode lifetimes $(t_{1/2})$ were measured at a constant current density of 125 mA/cm^2 . Under these conditions the BAPD device showed a lifetime of 140 h at an initial luminance of $L_0=4800 \text{ cd/m}^2$ (see Fig. 7.4b). In contrast, the F_4TCNQ -doped device showed a shorter lifetime of 122 h at an initial luminance of $L_0=3350 \text{ cd/m}^2$. Calculated with an extrapolation factor [96, 97] n =1.5, the lifetimes at an initial luminance of 500 cd/m^2 are estimated to be 4200 h for BAPD-doped devices and 2100 h for F_4 TCNQ-doped devices, respectively. The extrapolation factor n is basicly the ratio between the OLED lifetime and the logarithm of the initial luminance of the device. Since it has been shown that this ratio is more less constant [96, 97], one does lifetime measurements for time saving reasons at very high initial luminances followed by an extrapolation of the lifetime for less intense luminaces. The improvement in device lifetime can be a result from the reduced diffusion of BAPD and/or from the better charge-carrier

balance.

7.5. Doping and diffusion investigation by UPS and XPS

In order understand the basic behavior of BAPD and F_4TCNQ in organic electronic devices, I have initiated ultraviolet photo emission spectroscopy (UPS, He I, 21.22 eV) and X-ray photo emission spectroscopy (XPS, Al K α , 1486.6 eV) investigations. The UPS and XPS spectra itself were measured by Dr. Sabine Hirth (BASF analytics department). However, the preparation of the samples (explained in the following) as well as the analysis and interpretation of the UPS and XPS spectra were done by myself.

The doping strength of BAPD and F_4TCNQ was investigated on two different samples of type A (Fig. 7.5a and 7.5b): a 10 nm thick α -NPD layer, doped with 5 weight% of BAPD or F_4TCNQ , respectively. The doped layers were evaporated ontop of a Ag covered Si wafer. The HOMO level of a 30 nm undoped α -NPD layer, also evaporated ontop of a Ag covered Si wafer, acts as the reference (-1.52 eV below Fermi level ε_F). The stronger the dopant, the closer the HOMO level of sample type A will move to ε_F . The HOMOs of the BAPD- and F_4TCNQ -doped α -NPD layers are located at -0.89 eV and -0.57 eV with respect to ε_F . This means that BAPD acts as a p-dopant, but less strong than F_4TCNQ . This confirms the weaker electron-accepting properties of BAPD compared to F_4TCNQ , predicted by the lower calculated EA (*vide supra*).

Diffusion of dopants into the light emitting layer of OLEDs could decrease their lifetime due to exciton quenching [27]. This quenching process is caused by trapping of the electron at the ionized dopant. Therefore, I investigated the diffusivity of F_4TCNQ in comparison to BAPD by XPS and UPS. In the XPS analysis, the F(1s) core level intensities of a 10 nm thick pure F_4TCNQ layer, evaporated on a silicon wafer, were compared to samples in which this F_4TCNQ layer was covered by 30 nm of α -NPD. The measurements were carried out 24 hours after the evaporation, in order to get a realistic picture of the diffusivity of the dopant. The amount of fluorine present on top of the 10 nm thick pure F_4TCNQ layer was measured to be $(10.6 \pm 0.3)\%$. When the F_4TCNQ layer was covered by 30 nm of α -NPD, only $(0.2 \pm 0.1)\%$ of fluorine could be detected.

For BAPD, a comparable XPS investigation was difficult due to its elemental composition: In contrast to F_4TCNQ , BAPD contains no atoms which make the molecule clearly distinguishable from the α -NPD surface². To overcome this problem the diffusion of dopants was indirectly probed by UPS. This investigation was based on the fact, that UPS probes only the energetic conditions right at the

 $^{^{2}(4.6 \}pm 0.1)\%$ of oxygen atoms were found by XPS on all samples, caused by the air exposure during the sample transfer into the measurement set up. Therefore, is was not possible to distinguish between oxygen included in the BAPD molecule and oxygen originated from the air exposure.



Figure 7.4.: (a) Luminance vs. bias voltage and (b) lifetimes of 2 wt% F_4TCNQ and BAPD doped α -NPD/Alq₃-based OLED devices. The lifetime measurement data was acquired based on a constant current density of 125 mA/cm² for both device types.



Figure 7.5.: UPS measurements of the HOMO level with respect to the Fermi level $\varepsilon_{\rm F}$ of (a) 5% homogeneously doped α -NPD layers (sample type A) in comparison to doped layers additionally covered by 30 nm of undoped α -NPD (sample type B). The respective cutoffs followed the HOMO shifts accordingly. The Fermi energy $\varepsilon_{\rm F}$ of the UPS/XPS measurement setup was calibrated with reference to gold since this metal doesn't oxidize (see also Fig. 4.6). (b) Energy gap between $\varepsilon_{\rm F}$ and the HOMO of BAPD (F₄TCNQ)-doped B-type samples in relation to the doped A-type samples and the undoped α -NPD reference.

surface [98]. Studies on organic-organic interfaces (including F_4 TCNQ doped α -NPD) have shown, that the energy level alignment in these systems is determined by dipole formation, and not by molecular level bending [99]. Therefore we can be assured, that the energy levels of our measured surface are representative of those solely determined by doping concentration and not by any interface effects where internal fields are present (i.e., band bending).

I prepared two types of samples: 10 nm thick 5% homogeneously doped α -NPD layers (sample type A, vide supra) and samples where the doped layers were additionally covered by 30 nm of undoped α -NPD (sample type B, Fig. 7.5). As a reference an undoped 30 nm thick α -NPD layer was chosen. To relate the characteristic shifts of the energy levels of sample type A and B (see Fig. 7.5) to the diffusivity of the respective dopants, one has to understand the relation of the Fermi energy $\varepsilon_{\rm F}$ to the doping density N_A in the samples: The electron density in the conduction band of an intrinsic semiconductor is given by

$$n(T) = 2 \int_{E_{\rm CB}}^{\infty} g_{\varepsilon}^{CB}(\varepsilon') f_{\rm FD}(\varepsilon', \varepsilon_{\rm F}, T) \ d\varepsilon'$$
(7.2)

where g_{ε}^{CB} is the normalized density of states in the conduction band and $f_{\rm FD}(\varepsilon', \varepsilon_{\rm F}, T)$ is the Fermi-Dirac distribution function. Congruently, the hole density created by thermal excitations are given by

$$p(T) = 2 \int_{-\infty}^{E_{\rm VB}} D_{\varepsilon}^{VB}(\varepsilon') \left[1 - f_{\rm FD}\left(\varepsilon', \varepsilon_{\rm F}, T\right)\right] d\varepsilon' .$$
(7.3)

At ambient conditions, the valence electrons of an p-doped semiconductor are rather excited into the acceptor states $E_{\rm A}$ of the p-dopant than into the conduction band of the semiconductor. Thus, the normalized density of states g_{ε}^{A} of the acceptor states $E_{\rm A}$ of the p-dopant determines the electron density and Eq. (7.2) changes to

$$n(T) = 2 \int_{E_{\rm A}}^{\infty} g_{\varepsilon}^{A}(\varepsilon') f_{\rm FD}\left(\varepsilon', \varepsilon_{\rm F}, T\right) \, d\varepsilon' \,.$$
(7.4)

It has been reported for F_4 TCNQ doped amorphous hole transport layers [100], that doping concentrations < 3% lead to deep acceptor states E_A . Thus, the occupation probability of the respective states can be described in good approximation by Boltzmann statistics. Therefore, Eq. (7.3) and Eq. (7.4) can be written as

$$n(T) = \underbrace{2\int_{E_{A}}^{\infty} g_{\varepsilon}^{A}(\varepsilon') \exp\left(-\frac{\varepsilon' - E_{A}}{k_{B}T}\right) d\varepsilon'}_{\equiv n_{0}(T)} \cdot \exp\left(-\frac{E_{A} - \varepsilon_{F}}{k_{B}T}\right), \quad (7.5)$$

-

$$p(T) = \underbrace{2 \int_{-\infty}^{E_{\rm VB}} g_{\varepsilon}^{VB}(\varepsilon') \exp\left(-\frac{E_{\rm VB} - \varepsilon'}{k_{\rm B}T}\right) d\varepsilon' \cdot \exp\left(-\frac{\varepsilon_{\rm F} - E_{\rm VB}}{k_{\rm B}T}\right), \quad (7.6)$$

$$\underbrace{= p_0(T)}$$

and are considered to be also qualitatively applicable to describe organics. Assuming a very narrow density of acceptor states g_{ε}^{A} , the integral in Eq. (7.5) is similar to the doping density $N_{\rm A}$ $(n_0(T) \approx N_A)$. Since the semiconductors are electrical neutral, the relation n(T) = p(T) is valid. Therefore, using Eq. (7.5) and Eq. (7.6) the position of the Fermi level $\varepsilon_{\rm F}(T)$ within the organic semiconductor can be derived to

$$\varepsilon_{\rm F}(T) = \frac{E_{\rm A} + E_{\rm VB}}{2} + \frac{k_{\rm B}T}{2} \ln \frac{p_0(T)}{N_{\rm A}} \,.$$
(7.7)

If two samples (A and B) contains the same matrix molecule (in this case α -NPD) but different doping concentrations N_A^A and N_A^B of the **same** dopant, the energetic difference of their respective Fermi-levels $\varepsilon_F^A(T)$ and $\varepsilon_F^B(T)$ can be derived as

$$\varepsilon_{\rm F}^{\rm A}(T) - \varepsilon_{\rm F}^{\rm B}(T) = \frac{k_{\rm B}T}{2} \ln\left(\frac{N_{\rm A}}{N_{\rm B}}\right).$$
 (7.8)

Thus, the energetic difference of the Fermi-levels is only dependent on the respective doping densities. If BAPD and F_4 TCNQ would show the same diffusivity, the energy difference between the HOMO's of the respectively doped sample A and B should be identical according to Eq. (7.8). BAPD sample B shows a difference of 0.29 eV compared to BAPD sample A, whereas F_4 TCNQ sample B shows a difference of 0.18 eV compared to F_4 TCNQ sample A (Fig. 7.5). This 0.11 eV larger shift for BAPD sample B indicates that the surface of the BAPD sample B is less p-doped than the respective F_4 TCNQ sample B. Thus, it can be concluded that BAPD shows a reduced diffusivity through α -NPD compared to F_4 TCNQ.

7.6. Conclusion

In summary, the novel p-dopant 2,3-di(N-phthalimido)-5,6-dicyano-1,4benzoquinone (BAPD) was synthesized and compared to the state-of-the-art dopant F_4TCNQ . BAPD shows a significant higher evaporation temperature and thermal stability than F_4TCNQ . This can be an important advantage in handling and processing the material in mass-production. Furthermore, it was shown with precise UPS and XPS measurements, that the diffusion capability of BAPD was effectively lowered. Although BAPD is a less strong p-dopant than F_4TCNQ , the lower diffusion tendency and higher thermal stability of this new class of organic dopants forms an attractive potential for the lifetime improvement of organic electronic devices. Further improvements on the electron-accepting strength of this class of dopants are under way.

8. Development of a novel organic tandem cell architecture

Solar cells based on organic materials have potential advantages compared to traditional inorganic solar cells, such as lower production costs, their light weight and the processability on flexible substrates [101]. Despite enormous progress made in research with small-molecule [4, 5], dye-sensitized [102, 103, 104] and polymer solar cells [105, 106], none of these device concepts have fully reached the performance and technical maturity to enter the marketplace. A promising approach for improvement could be the superposition of two efficient organic solar cells with complementary absorption spectra [6]. This tandem cell architecture has certain advantages compared to single cells: Due to the complementary absorption of the subcells, the tandem cell can have a higher optical density over a wider spectral range than a single cell. Furthermore, as the two cells are connected in series, the open circuit voltage (V_{oc}) can be increased, in the best case, to the sum of both subcells.

So far, organic tandem cells have been realized for dye-sensitized devices [107, 108], for small-molecule solar cells [7, 8], for polymer- based devices [109, 110, 111] and for combinations of polymer and small-molecule concepts [112, 113]. Here, a novel all organic tandem cell concept based on a solid state dye-sensitized solar cell (sDSC) combined with a vacuum-deposited bulk heterojunction (BHJ) solar cell will introduced and discussed.

8.1. Device fabrication of the novel tandem solar cell

The structure of the fabricated tandem cell is schematically shown in Fig. 8.1b. On top of fluorine-doped tin oxide (FTO) coated glass substrates, I deposited a titanium dioxide blocking layer (b-TiO₂) by spray pyrolysis. This was followed by a nano-porous titanium dioxide (np-TiO₂) film prepared by spin coating a colloidal TiO₂ paste containing nanoparticles of 18 nm diameter. After the np-TiO₂ layer had been sintered it was sensitized with the indoline dye D102 [104] (Fig. 8.1a). The sDSC subcell was completed by spincoating the hole conductor matrix via a solution of 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'spirobifluorene(spiro-MeOTAD) in chlorobenzene. The hole conductor penetrates into the pores of the np-TiO₂ film and additionally forms an overstanding layer



Figure 8.1.: (a) Chemical structure, calculated electron affinity (EA) and ionization potential (IP) of the photo active materials used in the single and tandem devices. (b) Schematic device structure of an optimized tandem cell. The BHJ subcell is denoted in blue, the sDSC subcell is denoted in red.

on top. To add the bulk heterojunction (BHJ) subcell, the device was transferred into a high vacuum $(2 \cdot 10^{-6} \text{ mbar})$ system. First a Ag recombination layer was evaporated on top of the spiro-MeOTAD hole transport layer 0.6 Å/s, 2 nm). This was followed by the layer sequence Bphen (0.6 Å/s, 6 nm), C₆₀ (2 Å/s, 10 nm - 60 nm) and co-evaporated ZnPc:C₆₀ (2 Å/s, 10 nm - 60 nm). As indicated, the respective thicknesses of the organic layers where varied in order to find the optimal device setup. The co-evaporation of the zinc phthalocyanine (ZnPc) and C₆₀ will from interpenetrating networks as schematically shown in Fig. 1.3. As discussed in Chapt. 3.2, these so-called bulk heterojunctions can provide high currents which are essential for efficient solar cells. The silver counter electrode was evaporated on top of the organic layers (5 Å/s, 100 nm).

8.2. Device results

The open circuit voltage $V_{\rm oc}$, the short circuit current $I_{\rm sc}$, the fill factor FF and the power conversion efficiency η were obtained under simulated 100 mW/cm² AM 1.5 white light illumination with the measurement equipment described in chapter 4.2.4. To identify the best cell structure, I varied the thickness of all layers in each subcell. For an optimal tandem device setup (Fig. 8.1b), I obtained a fill factor, FF= $(54 \pm 1)\%$, a short circuit current, $I_{\rm sc} = (8.2 \pm 0.1) \text{mA/cm}^2$



Figure 8.2.: I-V curves of the indoline dye based sDSC device (dots), the ZnPc/C₆₀ based BHJ device (triangles) and the tandem cell (quadrats). For the BHJ device, I measured $I_{\rm sc} = (14.3\pm0.2){\rm mA/cm^2}$, $V_{\rm oc} = (550\pm10) {\rm mV}$ and a FF= $(54\pm1)\%$. This yields a power conversion efficiency $\eta_{\rm p} = (4.2\pm0.1)\%$. The sDSC cell had $I_{\rm sc} = (8.8\pm0.1){\rm mA/cm^2}$, $V_{\rm oc} = (810\pm10){\rm mV}$, FF= $(58\pm1)\%$ and an efficiency of $\eta_{\rm p} = (4.1\pm0.1)\%$.

and an open circuit voltage, $V_{\rm oc} = (1360 \pm 10) \text{mV}$, leading to a power conversion efficiency of $\eta_{\rm p} = (6.0 \pm 0.1)\%$. Fig. 8.2 shows the I - V curves and device data of a single ZnPc/C₆₀ based BHJ cell, an indoline dye based sDSC cell and the tandem cell. Comparing the observed $V_{\rm oc}$ of the tandem device with the $V_{\rm oc}$ of both subcells it becomes evident that they add up to the achievable optimum of 1360 mV. The short-circuit photocurrent of the stacked cells in an ideal tandem device is limited by the lowest of the two individual cells. Thus, the measured $I_{\rm sc} = (8.2 \pm 0.1) \text{mA/cm}^2$ of our tandem cell is close to the theoretical limit of $I_{\rm sc} = (8.8 \pm 0.1) \text{mA/cm}^2$ given by the sDSC subcell.

During the optimization process, I recognized that the device performance is heavily dependent on the thickness of the spiro-MeOTAD overstanding layer. If the overstanding spiro-MeOTAD layer is too thin or absent, the interface between the BHJ and sDSC subcells is defined by the extremely rough np-TiO₂ (Fig. 8.3a). This could lead to short circuits within the 66 nm thick BHJ subcell. Overstanding layers with a thickness greater than 150 nm cause high series resistances $R_{\rm s}$ between both subcells, resulting in a decrease of the FF and $I_{\rm sc}$ in the tandem device. I found that a 150 nm thick overstanding spiro-MeOTAD layer guarantees the best compromise between a smooth surface (Fig. 8.3b), providing a



Figure 8.3.: (a) Detailed SEM cross sectional (200 nm scale bar) image of a tandem device showing a suboptimal BHJ - sDSC interface. Due to the missing, or rather very thin, spiro-MeOTAD overstanding layer the interface is defined by the extremely rough np-TiO₂. This leads to a strong incident angle dependence optical response and short circuits in the BHJ subcells. (b) SEM cross sectional images of the complete (1 μ m scale bar) and a detailed (500 nm scale bar) part of the tandem device with optimized spiro-MeOTAD overstanding layer.

reliable serial connection between the two subcells and an undesirable increase of the series resistance $R_{\rm s}$ of the whole device. Furthermore, the roughness of the spiro-MeOTAD layer has a direct influence on the absorption features of the BHJ subcell (discussed later).

8.3. Discussion of the incident-photon-to-current efficiency and absorption measurements

To compare the spectral response of the single cells with that of the corresponding subcells in the tandem device, I measured the incident-photon-to-current efficiency (IPCE) in the spectral range between 400 nm and 800 nm. Because in general the lowest $I_{\rm sc}$ of the two individual subcells limits the current of the complete device, I used bias light provided by red¹ or blue² LEDs in order to selectively activate the desired subcell. The cell which was not addressed by the background light could now be characterized by a sweep of monochromatic probe light through the entire visible spectrum with a resolution of 10 nm. For the characterization of the single cells I used white³ LED light for background illumination.

The complementary absorption of the single cells (Fig. 8.4) is reflected in maximum IPCE values of 71% at 450 nm for the sDSC cell and two dominant peaks with values of 80% at 610 nm and 76% at 680 nm for the BHJ cell. In the tandem device, the sDSC subcell shows similar IPCE values compared to the single device. However, the spectrum of the BHJ subcell differs from the corresponding single cell. Between 400 nm and 600 nm, the absorption feature is reduced by the indoline dye in the sDSC subcell (Fig. 8.4b). Most of the incident light is absorbed by the indolene dye D102 (structure shown in Fig. 8.1a) and therefore it cannot generate excitons in the BHJ subcell. The loss of the IPCE at wavelengths greater than 600 nm has its origin in the optical interference pattern within the device: As the thickness of the BHJ subcell is in the order of the wavelength of the incident light, the optical interference pattern becomes important for the cell performance [114]. The optical standing wave has to have the maximum within the 40 nm of the co-evaporated $ZnPc/C_{60}$ layer to convert the incoming photons most effectively into excitons. Thus, two loss mechanisms could be attributed to the present tandem cell device setup:

- 1. Due to the huge thickness of the sDSC top cell compared to the BHJ subcell, internal reflectances and small, but still present, absorption at wavelengths greater than 600 nm lead to a decrease of the light intensity within the BHJ subcell. As a result, the IPCE value decreases.
- 2. Despite the fact that the surface of the spiro-MeOTAD overstanding layer can be controlled by its thickness, it is still much rougher than the ITOcovered glass substrate which leads to an incident-angle dependent optical response of the BHJ subcell [115, 116]. This reduces the IPCE value.

 $^{^1\}mathrm{Red}$ LED (AlGalnP) with a luminous intensity of 8 cd and a peak emission wavelength of 630 nm.

 $^{^2\}mathrm{Blue}$ LED (InGaN) with a luminous intensity of 4.6 cd and a peak emission wavelength of 472 nm.

³White LED (GaN/InGaN) with a luminous intensity of 18 cd.



Figure 8.4.: (a) Incident Photon to Current Efficiency (IPCE) of the single and tandem devices. The single cell measurements were done under white light background illumination; the tandem device was illuminated with LED's of 472 nm and 630 nm peak emission wavelength, respectively. (b) Normalized absorption spectra of a solid state dye-sensitized (sDSC) solar cell and a vacuum-deposited bulk heterojunction (BHJ) solar cell.
Further work is aimed at improving the processing condition of spiro-MeOTAD in order to have a better roughness control of the overstanding layer.

8.4. Conclusion

In conclusion, it was demonstrated that an efficient organic tandem cell can be prepared from a solid state dye-sensitized solar cell combined with a vacuumdeposited bulk heterojunction solar cell. The complementary absorption of the dyes, as well as an adequate serial connection of both subcells, leads to a high power conversion efficiency of $\eta_{\rm p} = (6.0 \pm 0.1)\%$ under simulated 100 mW/cm² AM 1.5 illumination. By introducing the sDSC device concept as a candidate for a tandem cell, a large variety of dyes can be used which were not considered so far. This opens up many promising opportunities of increasing the efficiency of organic tandem solar cells in the future.

9. Summary

The development of efficient organic solar cells could be one approach to provide mankind with cheap, sustainable and ecofriendly energy.

The introduction of bulk heterojunction [4, 5] and tandem device architectures [6, 7, 8, 9] led recently to devices with power conversion efficiencies close or even higher than $\eta = 6\%$, showing the potential of organic photovoltaics. Nevertheless, to compete for the foreseeable future to inorganic solar cell technologies, the power conversion efficiencies of organic solar cells have to rise further in the range of 10 % into 15 %. Since the functioning of organic photovoltaics is based on a complex interplay of the electronic properties of its molecular components, it is desirable for an efficient evolution, to identify structural and energetical key characteristics of the molecular components that can lead to efficiency gains. Furthermore, there are virtually no limits for the synthesis of new photoactive materials for the use in organic photovoltaics. Therefore, it is crucial for the device fabrication as well as under a chemical point of view, to narrow potentially promissing classes of molecules and their derivatives under certain physical criteria.

One aim of this study was to find and identify so far unknown design criteria for molecules providing high efficiencies in organic solar cells. Thus, the question was raised: What is the physical cause for the differing performance of various metal-phthalocyanines (MPc's with M = Zn, Cu, Ni, Fe) in organic solar cells. Therefore, MPc/C_{60} based bilayer heterojunction solar cells were fabricated showing a clear dependence of the optimal layer thickness and overall performance on the employed MPc material. Initially, the origin of these differences were explored through structural analysises by AFM and high resolution XRPD measurements on powder and evaporated thin films. In the course of these measurements it was found, that all MPc's exhibit a similar thin film crystal structure. Furthermore, the relation between the known crystal structure of α -CuPc [17] and the molecular packing of vacuum deposited thin films was clarified which was described incorrectly in previous publications [64, 65, 66]. The optical properties of the metal phthalocyanines were investigated by solid state fluorescence and absorption measurements. While the MPc molecules under study had similar absorption characteristics, they differed markedly by their fluorescence spectra. Based on this finding, the lowest excited states of the MPc series were explored by correlated multi-reference ab inito calculations. An increasing number of excited states was obtained energetically below the initially excited ligand-based $\pi - \pi^*$ state (Q-band) going from ZnPc (zero) \rightarrow CuPc with one \rightarrow NiPc with two \rightarrow FePc with over six excited states. These states are induced by the interaction of ligand and metal orbitals. An increasing number of intermediate states lead to increasing rates for non-radiative relaxation of photoelectrically active excitons. This directly affects the lifetime and therefore the diffusion lengths $L_{\rm ex}$ of these excitons in the present MPc series. Thus, the effect offers a straightforward explanation for the experimentally observed reduced device performances from ZnPc to FePc.

A high open circuit voltage $V_{\rm oc}$ of a solar cell is a prerequisite for high efficiencies. Unfortunately, the $V_{\rm oc}$ of small molecule based organic solar cells is usually considerably lower than the HOMO-LUMO offset of the device, which determines the theoretical maximum of the V_{oc} in a first approximation. Thus, the question was investigated: What causes the difference between the possible open-circuit voltage and the actual measured voltage and how can this difference be reduced? To answer this question, heterojunction solar cells were produced containing ZnPc or one of the novel synthesized Phenyl-ZnPc, Naphtyl-ZnPc or Anthracenyl-ZnPc as p-conducting and C_{60} as n-conducting organic layers. By adding the respective aryl substituents to the ZnPc core, the polarizability α of the molecules was successively increased. Concurrently, an increase of the $V_{\rm oc}$ from 550 mV to 790 mV by using the highly polarizable Anthracenyl-ZnPc instead of ZnPc was achieved. Quantum mechanical calculations, simulating the charge separation mechanism at the DA-interface of Phenyl-ZnPc/ C_{60} and Naphtyl-ZnPc/ C_{60} showed, that the interplay between characteristic packing and polarization effects could lead to considerably different Coulomb interactions of the electron-hole pairs at the DA-interface. Thus, the experimental and theoretical observations strongly imply, that the increase of $V_{\rm oc}$ in the fabricated heterojunction solar cells in the order $ZnPc \rightarrow Phenyl-ZnPc \rightarrow Naphtyl-ZnPc \rightarrow$ Anthracenyl-ZnPc is mainly based on different Coulomb interactions induced by characteristic polarization effects of the respective molecules at the DA-interface. Based on these findings, a high molecular polarizability might be one important property for the design of active materials for high efficient organic solar cells.

The control of the conduction type and Fermi-level of semiconductors is crucial for the realization of all optoelectronic devices. In inorganic as well as in organic devices this can be achieved by defined doping of appropriate areas within the device. Unfortunately, organic dopants have the disadvantage, that they show a tendency to diffuse. This diffusion precludes the fabrication of interface-only doped devices because dopants could penetrate into other layers of the device and thereby change their composition and electrical properties. Furthermore, the evaporation rates of commercially free available organic dopants, e.g. F_4TCNQ , are difficult to control during the evaporation process. The reason for this are the very low evaporation temperatures caused by the small molecular size of the respective dopants. Thus, it has been investigated, how the molecular structure of a dopant should be in order to reduce its diffusivity and increase the evaporation temperature to allow a more efficient processing of the compound. As a result, the novel p-dopant 2,3-di(N-phthalimido)-5,6-dicyano-1,4-benzoquinone (BAPD) was synthesized and compared to the state-of-the-art dopant F_4TCNQ . Here, BAPD showed a significant higher evaporation temperature and thermal stability than F_4TCNQ . This can be an important advantage in handling and processing the material in mass production. Furthermore, it was shown with precise UPS and XPS measurements, that the diffusion capability of BAPD was effectively lowered. Although BAPD is a less strong p-dopant than F_4TCNQ , the lower diffusion tendency and higher thermal stability of this new class of organic dopants forms an attractive potential for the use in organic electronic devices. Further improvements on the electron affinity strength of this class of dopants are under way.

In addition to basic and applied physical questions, I worked on the development of new, efficient solar cell architectures during my PhD thesis. In the course of this work it could be shown, that an efficient organic tandem cell can be prepared from a solid state dye-sensitized solar cell combined with a vacuum-deposited bulk heterojunction solar cell. The complementary absorption of the dyes, as well as an adequate serial connection of both subcells, leads to a high power conversion efficiency of $\eta_p = (6.0 \pm 0.1)\%$ under simulated 100 mW/cm² AM 1.5 illumination. By introducing the sDSC device concept as a candidate for a tandem cell, a large variety of dyes can be used which were not considered so far. This opens up many promising opportunities of increasing the efficiency of organic tandem solar cells in the future.

10. Deutschsprachige Zusammenfassung

Die Entwicklung von effizienten organischen Solarzellen kann ein Ansatz für eine billige, nachhaltige und umweltfreundliche Energieversorgung der Menschheit darstellen.

Mit organische "Bulk-Heterojunction"- [4, 5] und Tandem-Solarzellen [6, 7, 8, 9] konnten bereits Effizienzen um $\eta = 6\%$ erreicht werden, was das Potential der organischen Photovoltaik belegt. Um auf absehbare Zeit konkurenzfähig zu anorganischen Technologien zu werden, müssen die Effizienzen von organischen Solarzellen in den Bereich von 10% bis 15% gesteigert werden. Da die Funktionsweise von organischen photovoltaischen Bauteilen auf einem komplexen Zusammenspiel der elektronischen Eigenschaften verschiedenster Moleküle basiert, ist es für eine effiziente Weiterentwicklung notwendig, strukturelle sowie energetische Schlüsseleigenschaften der molekularen Komponenten zu identifizieren, die zu einer nachhaltigen Effizienzsteigerungen führen können. Weiterhin sind der Synthese von neuen Materialien für die organische Photovoltaik nahezu keine Grenzen gesetzt. Aus diesem Grund ist es nicht nur für den Zellenbau sondern auch aus chemischer Sicht wichtig, potentiell vielversprechende Molekülklassen und deren Derivate unter bestimmten Kriterien einzugrenzen.

So wurde die Frage aufgegriffen, was die grundsätzlich physikalische Ursache für die unterschiedliche Leistungsfähigkeit von verschiedenen, in der organischen Photovoltaik weit verbreiteten Metall-Phthalocyanine (MPc's mit M = Zn, Cu, Ni, Fe) in organischen Solarzellen ist. Dabei wurden zunächst MPc/C_{60} basierende "Heterojunction"-Solarzellen hergestellt. Diese zeigten eine klare Abhängigkeit der optimalen Schichtdicken als auch der Zelleffizienzen von den verwendeten Metall-Phthalocyaninen. Die Ursache für diese Unterschiede wurde als erstes durch Strukturanalysen anhand von AFM und hochauflösende XRPD Messungen an Pulver und aufgedampften dünnen Schichten untersucht. Im Zuge dieser Messungen wurde herausgefunden, dass alle Metall-Phthalocyanin Filme eine gleichartige Struktur haben. Weiterhin wurde der Zusammenhang zwischen der bekannten Kristallstruktur von α -CuPc [17] und der molekularen Packung in aufgedampften Filmen klargestellt. Dieser Zusammenhang wurde in vorangegangenen Publikationen falsch beschrieben [64, 65, 66]. Die optischen Eigenschaften der verschiedenen Metall-Phthalocyanine wurde mit Hilfe von Festkörper-Fluoreszenz- und Absorptions-Messungen untersucht. Dabei wurde festgestellt, dass im Gegensatz zu den sehr ähnlichen Absorptionseigenschaften große Unterschiede in den Fluoreszenz-Spektren zu beobachten sind. Auf Grund dieser Entdeckung wurden die niedrigsten Anregungszustände der MPc-Serie mit Hilfe von korrelierten Multi-Referenz ab initio Rechnungen untersucht. So konnte eine steigende Anzahl von angeregten Zuständen, ausgehend von ZnPc(null) \rightarrow CuPc(einem) \rightarrow NiPc(zwei) \rightarrow FePc (>sechs) angeregten Zuständen, energetisch unterhalb der ursprünglich angeregten Liganden basierten $\pi - \pi^*$ Zuständen (Q-band) aufgezeigt werden. Diese Zustände werden durch Wechselwirkungen zwischen Liganden- und Metallorbitalen induziert. Eine steigende Anzahl dieser Zwischenzustände führt zu einem Anstieg der strahlungslosen Deaktivierung von optisch angeregten Exzitonen. Das wiederum beeinflusst direkt die Lebensdauer und damit die Diffusionslänge $L_{\rm ex}$ dieser Extionen in der vorliegenden MPc-Serie. Dieser Sachverhalt bietet eine direkte Erklärung für die experimentell beobachtete sinkende Effizienzen von ZnPc basierten Solarzellen zu FePc basierten Solarzellen.

Eine hohe Leerlaufspannung $V_{\rm oc}$ ist eine Grundvoraussetzung für hohe Effizienzen einer Solarzelle. Unglücklicherweise ist die $V_{\rm oc}$ von organischen Solarzellen oft deutlich kleiner als der HOMO-LUMO-Offset innerhalb der Zelle, welcher in erster Nährung das theoretische Maximum der Leerlaufspannung bestimmt.

Es wurde der Fragestellung nachgegangen, welche Ursache die Differenz zwischen der möglichen Leerlaufspannung und der tatsächlich gemessener Spannung hat und wie diese Differenz reduziert werden kann. Um diese Frage zu beantworten, wurden zunächst "Heterojunction"-Solarzellen hergestellt. Diese enthielten ZnPc bzw. jeweils das neuentwickelte und synthetisierte Phenyl-ZnPc, Naphtyl-ZnPc oder Anthracenyl-ZnPc als p-Leiter und C₆₀ als n-Leiter. Durch das definierte Anfügen von immer größeren Aryl-Substituenten an den ursprünglichen ZnPc-Kern wurde die Polarisierbarkeit α der entsprechenden Moleküle sukzessiv erhöht. Zug um Zug konnte so durch die Benutzung des hoch polarisierbaren Anthracenyl-ZnPc anstatt des reinen ZnPc die Leerlaufspannung der entsprechenden Solarzellen von 550 mV auf 790 mV erhöht werden. Quantenmechanische Berechnungen, die die Ladungstrennung an der DA-Grenzfläche von Phenyl-ZnPc/C₆₀ und Naphtyl-ZnPc/C₆₀ simulieren, zeigten, dass das Wechselspiel zwischen der molekülcharakteristischen Packung und Polarisationseffekten zu deutlich unterschiedlichen Coulombwechselwirkungen der Elektron-Loch Paare an der DA-Grenzfläche führen können. So implizieren die experimentellen und theoretischen Beobachtungen, dass der Anstieg der Leerlaufspannung $V_{\rm oc}$ in den hergestellten "Heterojunction"-Solarzellen in der Reihenfolge der benutzen p-Leiter von $ZnPc \rightarrow Phenyl-ZnPc \rightarrow Naphtyl-ZnPc \rightarrow Anthracenyl-ZnPc$ hauptsächlich auf unterschiedliche Coulombwechselwirkungen, ausgelöst durch charakteristische Polarisierungseffekte der entsprechenden Moleküle an der DA-Grenzfläche zurückzuführen sind. Basierend auf diesen Forschungsergebnissen könnte die molekulare Polarisierbarkeit eine bedeutende Design-Eigenschaft für photoaktive Materialien für hocheffiziente organische Solarzellen sein.

Die Realisierung von stabilen und reproduzierbaren pn-Übergängen, welche

den Grundbaustein für fast alle heutigen elektronischen Geräte darstellen, war und ist von entscheidender Bedeutung. In anorganischen wie auch in organischen Bauteilen kann dies durch gezieltes Dotieren von entsprechenden Bereichen bzw. Schichten erreicht werden. Dabei zeigen organische Dotanten den großen Nachteil, dass sie auf Grund ihrer kleinen molekularen Größe nicht an Ort und Stelle bleiben, sondern in dem entsprechenden Bauteil diffundieren. Weiterhin sind die Aufdampfraten der kommerziell frei verfügbare organischen Dotanten wie F_4TCNQ während des Verdampfungsprozesses schwer zu kontrollieren, da durch die geringe Größe die Verdampfungstemperatur sehr niedrig liegt. So wurde der Frage nachgegangen, wie die molekulare Struktur eines Dotanten aussehen muss, um seine Diffusivität zu verringern und die Verdampfungstemperatur zu erhöhen um eine effizientere Verarbeitung zu ermöglichen. Resultierend aus diesen Uberlegungen wurde der neuartige p-Dotant 2,3-di(N-phthalimido)-5,6dicyano-1,4-benzoquinone (BAPD) synthetisiert und mit dem gängigen p-Dotant F_4 TCNQ verglichen. Dabei zeigte BAPD eine deutlich erhöhte Verdampfungstemperatur und thermische Stabilität als F₄TCNQ. Das kann ein wichtiger Vorteil bei der Verarbeitung und Handhabung dieses Materials in der Massenproduktion Weiterhin wurde mit präzisen UPS und XPS Messungen gezeigt, dass sein. die Diffusionseigenschaften von BAPD effektiv verringert wurden. Obwohl sich herausstellte, dass BAPD ein schwächerer p-Dotant als F_4 TCNQ ist, stellt die höhere thermische Stabilität und die niedrigere Diffusivität ein attraktives Potential für den Einsatz in der organischen Elektronik dar. Darüber hinaus wird an einer weiteren Verbesserung der elektronenziehenden Eigenschaften dieser Dotantenklasse gearbeitet.

Neben physikalischen Fragestellungen habe ich mich während meiner Promotion auch mit der Suche und Entwicklung von neuen, effizienten Solarzellen-Architekturen beschäftigt. Im Zuge dessen konnte gezeigt werden, dass eine effiziente organische Tandemzelle basierend auf einer Kombination aus einer Feststoff farbstoffsensibilisierten Solarzelle (sDSC) und einer vakuumverdampften "Bulk-Heterojunction"-Solarzelle realisiert werden kann. Die komplementäre Absorption der Farbstoffe als auch die hinreichend gute serielle Verbindung der beiden Subzellen führte zu einer hohen Effizienz von $\eta_{\rm p} = (6.0 \pm 0.1)\%$ unter simulierter 100 mW/cm² AM 1.5 Beleuchtung. Durch die Einführung der sDSC Solarzelle als ein möglicher Kandiat für Tandemzellen können nun eine Großzahl von Farbstoffen benutzt werden, die bisher nicht in Betracht gezogen wurden. Dies eröffnet zahlreiche vielversprechende Möglichkeiten zur Steigerung der Effizienzen von zukünftigen organischen Tandem-Solarzellen.

A. Detailed experimental information for chapter 5

A.1. High resolution X-ray powder diffraction

A.1.1. Sample preparation and measurement setup

Fe,Ni,Cu and Zn-Phthalocyanine layers of 30 nm and 1 μ m thickness were vacuum deposited (2 · 10⁻⁶ mbar) with a rate of 2 Å/s on precleaned ITO covered glass substrates. High resolution X-ray powder diffraction patterns of thin films were recorded at room temperature. A laboratory powder diffractometer (D-8, Bruker, Cu-K- α_1 radiation from primary Ge(111) Johannson monochromator; LynxEye position sensitive detector (PSD) with an opening angle of 3°) in Bragg-Brentano mode was used. The sample was loaded on a plexiglas sample holder with a 2 mm deep cavity of 32 mm diameter. The samples were aligned such to minimize sample height errors and rotated during measurement for better particle statistics. Data were generally taken in steps of 0.009° 2 Θ from 2.0° 2 Θ - 62.0° 2 Θ at a scanning speed of 0.5°/minute.

A.1.2. Sample height correction

To account for the small but (almost) unavoidable sample displacement error, a glass substrate with a sole ITO thin film was aligned carefully in a previously calibrated sample holder and used as reference standard. The (222) reflection as the strongest reflections of ITO turned out to be largely insensitive to peak shifts and could thus be used as a suitable reference for correcting the sample height error. This approach is based on the assumption that the position of the (222) reflection of ITO is constant throughout all samples under investigation which seemed to be reasonable [117]. The calculated cubic lattice parameter was fixed to 10.28104 Å. LeBail fits [61] using exclusively the (222) reflection of ITO for all samples containing ITO, immediately revealed individual sample displacement parameters and allowed the angular correction of the reflections of the different phthalocyanine samples.

A.1.3. Determination of domain size

The fundamental parameter (FP) approach [118] was used to describe the peak profile of our 1 μ m and 30 nm thick evaporated MPc films using direct convo-

lutions of wavelength distribution, the geometry of the diffractometer and the microstructural properties like domain size and microstrain. Due to the fact that the geometry of the LynxEye position sensitive detector is not fully characterized by FP's, fine tuning of the available parameters was performed by using refined values of the FP's from a precise measurement of the NIST line profile standard SRM 660a (LaB₆) measured in a silicon (911) low background sample holder over the full 2Θ range of the diffractometer.

A.2. Estimating the grain size from the AFM images

The morphology of 30 nm thick films of different metal phthalocyanines vacuum deposited on ITO coated glass was investigated with an atomic force microscopy (AFM) with Si-tips (resonance frequency 68 kHz, force constant 1,3 N/m) used in tapping mode. As shown in Fig. 5.4, the used ITO is very smooth (RMS = 0,48 nm) but with height differences of up to 3 nm not completely flat. This influences the further film growth of the organic materials, resulting in dints in the Pc film (Fig. 5.4). All Pc's show a similar topography and their crystallite sizes are only slightly different. For estimating the grain size from the AFM images a threshold method was used. First, the images were flattened with a third grade polynomial fit. Only structures higher than the threshold level of the geometrical mean were taken into account and the average diameter d of their 2D projection was calculated.

A.3. Fluorescence measurement technique

Due to the in general low fluorescent quantum yield of the measured phthalocyanines the smallest and almost unavoidable amount of fluorescence light coming from impurities became significant. To get still a clear and reliable measurement signal the ZnPc and CuPc films were exposed with a 532 nm laser which describes a significant shift to the maximum absorption regime of the respective phthalocyanines. Using this technique it was possible to avoid overlap coming from parasitaric impurities within the phthalocyanine films by shifting their fluorescence peaks to shorter wavelength than the fluorescence of the MPc's.

A.4. Method for quantum state calculations

The metal basis set was triple- ζ quality with polarization functions (TZVP [119]). The ligand heavy atoms were treated with a split valence basis and polarization functions, while hydrogens do not carry polarization functions (SV(P) [119]). This basis set leads to overall 625 basis functions, and is expected to give qualitatively meaningful results in a correlated ab initio calculation.

Geometry optimizations were carried out under D_{4h} symmetry constraints at the B3LYP [120, 121, 122]density functional theory (DFT) level, using TURBO-MOLE, v5.10 [123]. All molecules were optimized in the respective ground states that are indicated in the main text.

The multireference-configuration-interaction (MRCI) calculations were done with the spectroscopy oriented CI (SORCI [67]) procedure as implemented in ORCA [124].

The reference wave functions were built by the complete-active-space (CAS) technique, involving the relevant frontier orbitals n, containing m electrons - CAS(n,m) - of the molecule under study. In order to keep the MR-CI calculation tractable and balanced, CAS(n,m) was chosen to be for ZnPc: CAS(2,3); CuPc: CAS(3,4); NiPc: CAS(8,7); FePc: CAS(8,7).

The initial orbitals for the MR-CI calculation were quasi-restricted orbitals from an unrestricted DFT calculation, obtained at the B3LYP [120, 121, 122] level. This approach leads in the present case to the expected energetic order of the relevant orbitals (the metal d-block and the ligand a_{1u} and e_g orbitals), that were chosen to belong to the active space. Also Hartree-Fock orbitals were used as initial orbitals, however, this made it necessary to re-order the relevant orbitals in the definition of the active space of the MR-CI procedure (see above). The energies of the resulting MR-CI excited states agrees between both alternatives to within 0.1 eV.

In all MRCI calculations, the thresholds T_{sel} , T_{pre} and T_{nat} defined previously [67] and introduced to enhance computational efficiency at small loss of accuracy were set to 10^{-6} Eh, 10^{-4} Eh and 10^{-5} Eh, respectively.

A.5. Detailed information of the calculated excited states

It was demonstrated already in early theoretical work, e.g. on CuPc [125], that exchange coupling of the metal center with ligand states gives rise to spin-allowed transitions at low energy [68], i.e. a doublet (tripdoublet) [126] state in CuPc. Results from ultrafast spectroscopy indicate that this state is responsible for efficient fluorescence quenching [127].

While there are a number of more recent theoretical studies on the excited states of MPc's [128, 129, 130, 131, 132, 133, 134, 135, 136, 137], a rigorous theoretical treatment of the ligand-metal exchange coupled states (LMEC states) is lacking to this date. Herein, the low-energy LMEC states were calculated by an ab initio multi-reference configuration interaction technique (MR-CI) [138], specifically the Spectroscopy-Oriented CI (SORCI) approach by Neese [67]. The calculations explicitly take into account double-excitations and multi-configurational mixing. In the case of FePc, NiPc, and CuPc, LMEC states are located energetically well below the Q-band excitation on the phthalocyanine ligand at around 1.7 eV. Because the oscillator strength of a transition from ground state to the LMEC state is zero, the corresponding absorption features are not obvious. However, it is important to note that the LMEC states considered here are of the same spin as the respective ground states. Therefore, they may be populated on the femto- to picoseconds timescale by internal conversion from the initial ligand excited state. This process is expected to lead to a fast de-population of the initial excited state, and could therefore influence effectively the solid state fluorescence of the corresponding MPc's.

A.5.1. FePc

The leading ground state configuration obtained for FePc is a triplet, ${}^{3}A_{2g}$, with two unpaired electrons occupying the degenerate $1e_{g}$ (d_{xz} , d_{yz}) set of orbitals located on the metal. The first two excited states are d-d transitions and are low in energy, 0.13 eV and 0.69 eV. The three low-lying metal d-d states may couple to both the ligand $a_{2u} \rightarrow 2e_{g}$ singlet and triplet excitations, giving rise to a total of nine possible LMEC triplet states. In the energy range up to 1.7 eV four such configurations were obtained ; the assignments are given in table 5.4. Interestingly, the coupling of the first excited d-d state ($a_{1g} \rightarrow 1e_{g}$) to the ligand excitations obviously leads to a larger exchange stabilization, hence, all of the three possible corresponding triplet LMEC states (${}^{3}A_{2u}$) have been obtained below 1.7 eV. Due to limitations in the current implementation, higher roots of the CI we have not been calculated.

A.5.2. NiPc

NiPc has a closed shell ground state, ${}^{1}A_{1g}$, because the metal $1e_{g}$ are completely filled. A singlet d-d excited state $a_{1g} \rightarrow b_{1g}$ is predicted at 2.50 eV, even slightly below the Q-band transition. The corresponding (spin-forbidden) triplet ³d-d state is obtained at 0.82 eV. The (spin-forbidden) triplet ligand excited state $a_{1u} \rightarrow 2e_{g}$ is calculated at 1.47 eV. Three terms arise from the ligand triplet coupling to the metal triplet ³d-d state: quintet, triplet and singlet. The singlet component, ${}^{1}E_{u}$, is calculated at 2.17 eV. Hence, the calculations predict two states below the Q-band excitation (at 2.60 eV), which both belong to the singlet manifold: the d-d state ${}^{1}B_{1g}$, and the LMEC state ${}^{1}E_{u}$.

A.5.3. CuPc

In CuPc, the ground state spin is a doublet, with one unpaired electron residing in the Cu b_{1g} orbital. Exchange coupling of the ligand excited states $a_{1u} \rightarrow 2e_g$ to the singly occupied metal orbital gives rise to one quartet and two doublet states [68], the tripdoublet and the singdoublet. The latter corresponds to the singlet excitation in the Pc ligand (the Q-band excitation), and is calculated at 2.70 eV. The tripdoublet is significantly stabilized, to 1.43 eV. Also the quartet state was calculated, which was obtained 20 cm⁻¹ higher in energy than the corresponding doublet. This is somewhat surprising, but may be due to differential configuration mixing of the quartet with other ligand excited configurations. [68]

A.5.4. ZnPc

The ${}^{1}E_{\rm u} [a_{1\rm u} \rightarrow 2e_{\rm g}]$ excited state is calculated at 2.5 eV (500 nm), which may be compared to the absorption maximum in gas phase at 1.9 eV [139] and the DFT values between 1.4 eV [135] to 2.0 eV [133] The blue-shift is typically observed with this methodology [67] and can be attributed to the neglect of higher excitations (T, Q, ...), as well as the limited basis set, which is only of valence double-zeta quality on the ligand atoms due to the high computational cost associated with the MR-CI method. No excitations are calculated below this state.

B. Detailed experimental information for chapter 6

B.1. Crystal structure determination of N-ZnPc

Green plate shaped crystals were grown by thermal sublimation at 420°C at pressure 10^{-6} mbar. The crystals were analyzed by synchrotron XRD at the beamline PX III at SLS in Basel. Data collection was performed with MAR225 CCD diffractometer equipped with Barter mirrors monochromated radiation ($\lambda = 0.71073$ Å). The analyzed crystal belongs to tetragonal crystal system with cell dimensions a =26.034(4), b = 26.034(4) and c = 15.240(3). The space group is I4(1)/a with Z = 8. A total amount of 34877 reflections were collected with 5168 unique reflections in the range from 2Θ min = 4.40 to 2Θ max = 52.92° at 100 K. The structure was solved by direct method and refined on F^2 using the full matrix least square method [140] (Fig. B.1a). All the non-hydrogen atoms were refined as anisotropic and the hydrogen were assigned using rigid model and refined as isotropic atoms. The final R factor is 0.0951 and weighted R factor 0.2375. The goodness of the fit for the solution is 1.056. Only very small single crystals were obtained by thermal evaporation which has likely an influence on the final quite high R factor: The thermally evaporated crystals were very small and poorly reflecting. Therefore, the final R factor remained quite high.

B.2. Crystal structure determination of Ph-ZnPc

Green plate shaped crystals were grown by thermal sublimation at 390°C at pressure 10^{-6} mbar. The crystals were analyzed by synchrotron XRD at the beamline PX III at SLS in Basel. Data collection was performed with MAR225 CCD diffractometer equipped with Barter mirrors monochromated radiation ($\lambda = 0.73000$ Å). The analyzed crystal belongs to triclinic crystal system with cell dimensions a = 3.8200(8), b = 15.330(3), c = 16.950(3), $\alpha = 66.99(3)^{\circ}$, $\beta = 89.45(3)^{\circ}$ and $\gamma = 87.16(3)^{\circ}$. The space group is P-1 with Z = 1. A total amount of 6616 reflections were collected with 3412 unique reflection in the range from 2Θ min = 5.02to 2Θ max = 59.64° at 100 K. The structure was solved by direct method and refined on F² using the full matrix least square method [140] (Fig. B.1b). All the non-hydrogen atoms were refined as anisotropic and the hydrogen were assigned using rigid model and refined as isotropic atoms. The final R factor is 0.0448 and weighted R factor 0.1177. The final goodness of fit is 1.041. The structure is still



Figure B.1.: (a) ORTEP drawing of N-ZnPc (50% thermal probability ellipsoids) with atomic numbering. (b) ORTEP drawing of Ph-ZnPc with atomic numbering.

preliminary due to problems in the anisotropic refinement of the non-hydrogen atoms. We believe that the problem is in the employed absorption correction and we will work on it before the structure will be send to Cambridge crystallographic database.

B.3. XRPD analysis

XRPD graphs of the thin films (30 nm) of ZnPc and its derivatives were recorded with PANalytica's X'Pert Pro MPD diffractometer employing Cu K_{α} radiation ($\lambda = 1,542$ nm) (Fig. B.2). Typical scanning program was from 3° to 60° (2 Θ) with a step size 0.017° and counting time 100 s/step. Polycrystalline ZnPc thin film shows a strong peak at 6.84° (2 Θ) which is assigned to (010) reflection of α -ZnPc. For the Ph-ZnPc thin film a broad and very weak peak at 6° (2 Θ) is detectable whereas no reflections were observed for N- and A-ZnPc thin films.

B.4. Polarizability calculations

The calculations were performed with the **Turbomole** program [141, 142], at the RI-BP86/def-TZVP level of density functional theory [143, 144]. After geometry optimization, single point calculations with convergence criteria of 10^{-8} Eh in energy and 10^{-7} for the change in electron density were carried out. Static polarizabilities were obtained from a subsequent time-dependent density functional theory calculation employing the ESCF module of **Turbomole**.



Figure B.2.: XRD scans of the thin films (30 nm) of ZnPc, Ph-, Nand A-ZnPc on ITO substrate in a logarithmic intensity scale. Peaks at 21.5° and 31.2° (2 Θ) represent the (211) and (222) reflections of the ITO, respectively.

B.5. Charge separation calculations

The energetics were calculated in the following way: For the charged molecules, the molecular electron density was calculated via density functional theory (DFT) for each molecule. Specifically the BP86 functional [145, 120] in combination with a split valence basis set (SV(P)), including polarization functions on all heavy atoms [119], was used. Following, the atom centered partial charges were derived by fitting the electrostatic potential of the density [146]. Electrostatic interactions between the charged molecules were then calculated classically via Coulombs law, where atom centered ESP charges were used, also derived from DFT calculations. The same point charges were subsequently used to quantum mechanically polarize the electron density of the remaining neutral molecules of the respective chain. This was achieved by adding the point charges to the one electron hamiltonian of the DFT calculation of the molecular aggregate using the same level of theory as above. The sum of the classical coulomb interaction energies and the total energies of the polarized DFT calculation give then the total electrostatic energy of the specific chain configuration. It is important to note, that an additional neutral ZnPc molecule has to be added at the ZnPc-end of the chain as a buffer. This is necessary to avoid energetical artefacts from a positive charge directly exposed to vacuum on one side. All calculations were carried out with the **Turbomole** program package [142, 141].

C. Synthesis of the novel dopant BAPD

A mixture of 2,3-dichloro-5,6-dicyano-benzoquinone (33.4 g, 147.1 mmol) and potassium phthalimide (54.5 g, 294.2 mmol) in acetonitrile (500 ml) was stirred under reflux for 12 hours. The resulting deep brown suspension was filtrated. The solid was washed three time with warm water and one time with ethanol. After drying at 100°C under vacuum, a yellow solid was obtained (9.3 g, 14%). ¹H-NMR (D₂SO₄), $\delta = 7.6$ ppm; Maldi-MS: m/z= 447.9. Before device fabrication, BAPD was purified by gradient zone sublimation.

D. *IV*-characteristics of 64 organic solar cells on one substrate

See next page.



Figure D.1.: Measurement report generated by the automized measurement device described in Sec. 4.2.4 and shown in Fig. 4.5. The cell type which was measured here is a ZnPc/C_{60} bulk heterojunction solar cell. On the upper part of the report an overview of the cell yield on the substrate is given: All cells which had a 30% or lower efficiency in relation to the best working cell on the substrate are indicated black. All the other cells are indicated green. In the lower part the average cell characteristics as well as the best values of each quadrant on the substrate are given.

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i. Eidesstattliche Erklärung

Nach §19 Abs.6 DPO/AT erkläre ich hiermit an Eides statt, dass ich die vorliegende Promotion selbstständig und ohne unerlaubte Hilfe angefertigt habe. Es wurden keine anderen Quellen und Hilfsmittel benutzt als angegeben. Die aus Quellen wörtlich und inhaltlich übernommenen Stellen habe ich ausnahmslos kenntlich gemacht. Diese Arbeit hat in gleicher Form noch keiner Prüfungsbehörde vorgelegen.

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