2 Materials

This chapter introduces basic properties of the different material classes employed in this thesis. After a brief introduction into nano-sized semiconductors, conjugated polymers, carbon nanotubes and colloidal quantum dots will be discussed in more detail. This includes their basic properties with a focus on photophysical behaviour, as well as aspects of property modification. Important concepts necessary to understand these materials, such as excitons, triplets or charge carrier transport, will be introduced in the first section on organic solids and later on discussed specifically for CNTs and CQDs.

2.1 Nanoscale Semiconductors

The focus of this thesis lies on the study of nano-sized semiconducting materials. Unlike metals, for which the Fermi energy \( E_F \) lies within a band of allowed states, semiconductors exhibit \( E_F \) in a gap of their energy bands. Similar to insulators, this leads to a comparably small density of free charge carriers under equilibrium conditions (at finite temperature) – states below \( E_F \) are occupied and empty above. The distinction between insulators and semiconductors is arbitrarily chosen with respect to the width of the gap between the highest fully occupied band (valence band, VB) and the lowest fully unoccupied band (conduction band, CB). Typically, semiconductors are said to have a band gap smaller than 3 eV.

The density of states of an arbitrary semiconductor is shown in Figure 2.1 with respect to its dimensionality. A macroscopic or bulk semiconductor allows the charge carriers to move freely in all three spatial directions and one finds a square root shaped density of states (DOS) for the conduction- and the valence band respectively. If one dimension is drastically decreased, the carriers can only move freely in the two unchanged dimensions and are confined in the third. This geometry is said to be a quantum well (QW), which exhibits a stepwise constant DOS. Further confinement in a second dimension leads to the formation of quantum wires (QWR) and finally, if the confinement acts in every dimension, a zero-dimensional quantum dot (QD) is formed. Ideal QDs exhibit a discrete DOS spectrum and are therefore sometimes referred to as artificial atoms. Their discrete energy states are hence commonly denoted using the same formalism as for the quantum numbers of atoms. Typically, the confinement manifests strongest in...
2.2 ORGANIC SEMICONDUCTORS

Energy
Density of states
HOMO
HOMO-1
HOMO-2
LUMO
LUMO+1
LUMO+2
Conduction band
Valence band
1s
1s
1p
1p
1e
1e
CB
VB
C1
C2
V1
V2
Bulk
Quantum well
Quantum wire
Quantum dot
Molecule
EF

Figure 2.1: Density of states for an arbitrary semiconductor with respect to its dimensionality. From left to right, the confinement increases leading to a DOS that is proportional to $\sqrt{E}$ for the bulk material, a step-function for a quantum well and marked by van Hove singularities with an exponential decay for a quantum wire. Quantum dots and molecules on the right ideally exhibit discrete energy levels.

the separation of states close to the original band gap. Higher lying states lie increasingly close together and might be quasi-continuous.

Of these classes, quantum wires and quantum dots will be investigated in the form of carbon nanotubes and lead sulphide colloidal quantum dots. Additionally, the large class of organic semiconductors will be addressed, which exhibit discrete energy states as well, when isolated, as depicted on the right in Figure 2.1.

The critical length from which on confinement sets in is linked to the Bohr radius $r_B$ of the exciton describing the size of the formed electron hole pair.

$$r_B = \frac{\varepsilon_0 \varepsilon_r \hbar^2}{\pi m^* e^2},$$

(2.1)

where $\varepsilon_0$ and $\varepsilon_r$ are the permittivity of vacuum and the material and $m^*$ is the exciton effective mass. If the size of the nanocrystal is smaller than the Bohr radius in one direction (the characteristic length), confinement is present.

2.2 Organic Semiconductors

2.2.1 Conjugated Polymers

Organic materials are predominantly based on hydrogen and carbon atoms. Carbon, in its ground state, exhibits the electron configuration $1s^22s^22p^2$, i.e. two filled $s$-orbitals and two half occupied and degenerate $2p$-orbitals (Hund’s rule). In order to bind to the commonly found four partners, instead of just two as suggested from this configuration, one of the $2s$-electrons is
promoted into the unoccupied \( p \)-orbital and the atomic orbitals (AO) of carbon hybridise (mix). This process requires energy (Figure 2.2 (a)) that is significantly lower than what is freed when forming molecular bonds. In the simplest case of methane (\( \text{CH}_4 \)), for example, all outer electrons bind to one hydrogen atom, each then located in a molecular orbital (MO) shared between the atoms. These so-called \( \sigma \)-bonds exhibit their highest electron density between the C and H atom and the MOs arrange as a tetrahedron with an angle of 109.5° between them due to their mutual Coulomb repulsion (Figure 2.2 (b)). All four AO from C participating in these bonds are equal \( sp^3 \)-orbitals, each exhibiting 1/4 \( s \)-character and 3/4 of \( p \)-character.

Similarly, carbon can also form \( sp^2 \)- or \( sp \)-orbitals, the former of which represent the backbone of conjugated materials. In \( sp^2 \)-carbon, the three hybrid orbitals (with 1/3 \( s \)- and 2/3 \( p \)-character) lie in a plane (e.g. \( x \)-\( y \)), forming an equilateral triangle with an angle of 120° between them. The semi-occupied \( p_z \)-orbital aligns perpendicularly to this plane. In the simple case of ethene (\( \text{C}_2\text{H}_4 \)), for example, each carbon atom forms two \( \sigma \)-bonds via the \( sp^2 \)-electrons to hydrogen atoms and an additional \( \sigma \)-bond between the two carbons (Figure 2.2 (a)). The double bond between the carbon atoms stems from the two \( p_z \)-orbitals, which form overlapping molecular orbitals above and below the \( sp^2 \)-plane – so-called \( \pi \)-bonds. In contrast to electrons in the \( \sigma \)-bond, which are fixed between the two participating atoms, electrons in these \( \pi \)-orbitals are delocalised and can move freely in the \( \pi \)-system. These electrons are responsible for charge carrier conduction and related phenomena discussed throughout this thesis.

In a quantum mechanical picture, molecular orbitals \( \Psi_{\text{MO}} \) are formed approximately by the linear combination of all involved atomic orbitals \( \phi_i \) (LCAO)

\[
\Psi_{\text{MO}} = \sum_i c_i \phi_i, \tag{2.2}
\]

where \( c \) is a weighting factor. Depending on the sign (or phase) of the involved AO, binding or
anti-binding MO form. The latter are characterised by a lower energy and high probability of finding an electron between the atoms (consider Figure 2.3 (b) and (c), anti-binding orbitals are denoted with a star). Since anti-bonding orbitals exhibit zero probability of carriers in the centre between the atoms, these are typically more unstable than binding orbitals and their formation can give rise to bond dissociation. The highest molecular orbital occupied with electrons is called HOMO and the lowest unoccupied accordingly LUMO – together, they form the so-called frontier orbitals. Their difference in energy is typically associated with the band gap energy $E_g$ (although, strictly speaking, there are no bands present here). In most cases, $\pi$-bonds are responsible for the interaction of organic materials with light. The absorption of a photon promotes an electron from the $\pi$- to the $\pi^*$-orbital. For ethene, the difference in energy amounts to 6.7 eV. Increasing the number of carbon atoms involved, i.e. forming a chain with alternating single and double bonds, leads to an extension of the so-called conjugated $\pi$-electron system along the carbon backbone. Analogously to the particle in a box problem known from quantum mechanics, a longer chain (greater conjugation length) leads to states with a smaller energy separation.

For an infinite conjugation, this would lead to a HOMO and LUMO at the same energy, thus the formation of a semi-occupied band and the material, e.g. a polymer chain, would behave like a metal. Due to a redistribution of the bond lengths in such a system, however, this does not occur and the band gap opens to give the chain semiconducting properties (Peierls distortion). In real polymers, the actual chain is much longer than the conjugation length. This is due to defects and structural deformations. Torsion, for example, limits the overlap of the $p_z$-orbitals, for which only the parallel components overlap with each other in the $\pi$-bonds. A single polymer chain can thus include several distinct chromophores (conjugated segments).

Initial semiconducting polymers consisted of different arrangements of hydro-carbon chains
only. The prime examples are poly-acetylene (PA) and poly-phenylene vinylene (PPV), as depicted in Figure 2.4. In 2000, the Nobelprize in chemistry was awarded to Shirakawa, McDiarmid and Heeger for the observation that oxidation (i.e. p-doping) is possible for polyacetylene, which is considered a key moment of the research field into semiconducting polymers. The observation of charge transport through conjugated polymers was followed by growing research efforts into material synthesis as well as into their application. Throughout the 1990’s and early 2000’s, significant improvements in device performance, e.g. in organic solar cells, was achieved by using monomers involving heteroatoms. Oxygen, nitrogen or sulphur were for example used in materials such as MEH-PPV, MDMO-PPV, P3HT (Figure 2.4, left) More intricate hydrocarbon chains, such as in polyfluorene, also improved the device characteristics. Crucially, the side chains of these materials significantly increase their solubility in common solvents, facilitating their handling. Moreover, as will be discussed further below, the side chains strongly affect the morphology of formed films. In blends with the electron acceptor PCBM, the power conversion efficiency (PCE) of PPV-based materials was limited to about 3% – mostly due to its wide band gap (thus poor coverage of the solar spectrum) and a relatively low charge carrier mobility. Thiophene-based materials, especially poly(3-hexylthiophene) (P3HT), have been the working horses for organic photovoltaics (OPV) for a long time. Their typical PCE amounts to 3.5-4% and the record was set at 5.2%. The band gap of P3HT, at about 1.9 eV, is still not optimal, but the polymer exhibits good transport properties and is easy to process. Aforementioned materials (sometimes referred to as homopolymers) generally exhibit a band gap that is not smaller than approximately 2 eV. For photovoltaic purposes, however, a smaller gap would be beneficial. Development of new conjugated polymers has therefore often been driven by the desire to reduce the band gap in order to cover a broader range of the sun spectrum for applications in OPV.

Figure 2.4: Conceptual progress from purely CH-based semiconducting polymers as used in the 1970’s and 80’s (left top), first included the addition of sidechains to increase the polymer solubility and the insertion of heteroatoms in both the backbone and sidechain (left). Nowadays, electron rich and -poor groups (centre) are commonly used as building blocks in donor-acceptor polymers. Abbreviations explained in the glossary or main text.
As a remedy, heteropolymers or donor-acceptor (D-A) polymers have been synthesised, in which electron rich (donor) and -poor (acceptor) sub-units are coupled together (consider Figure 2.4 centre). As depicted in Figure 2.5, the orbitals of the two sub-units mix and form a gap that is smaller than the one of either sub-unit. In this way, the absorption onset of polymer films could be shifted from approximately 560 nm for MEH-PPV, 630 nm for P3HT to 830 nm in case of PCPDTBT (consider Figure 2.4 right). The incorporation of the D-A groups furthermore leads the HOMO to be predominantly located on the donor group and the LUMO on the acceptor group, which is assumed to be beneficial for exciton dissociation (vide infra).

Some important building blocks for D-A polymers are depicted in Figure 2.4. Common electron donor groups include polycarbozole (PC), which, together with the acceptor group benzothiadiazole (BTD) and a bridging thiophene, forms the material PCDTBT, currently often used to study basic properties in (opto)-electrical devices. In solar cells, it typically offers a PCE of 6-7%. A similar polymer, in which the BDT unit is connected with a bridged dithiophene instead of the carbozole, is PCPDTBT. This prototypical D-A polymer led to efficiencies of up to 5.5% and was studied extensively to understand excited state phenomena and the impact of spacer groups between the D and A group. Furthermore, as will be discussed in more detail in Chapter 4, it is possible to significantly improve the ordering of this material by replacing the bridging atom of the dithiophenes by silicon, to form Si-PCPDTBT (also known as PSBTBT).

Another acceptor group leading to promising performances of up to 8% is the diketopyrrolopyrrole (DPP) class of materials, often linked to thiophene rings. Recently, some of the new working horses have been D-A polymers based on the benzodithiophene coupled to thienothiophene units, such as in PTB7 or its variant PTB7-th, which will be employed in Chapter 5. Although these D-A materials achieved impressively high power conversion efficiencies in devices, they are often also prone to severe degradation upon illumination. This signifies that despite significantly improving key properties through chemical tailoring, the challenges involved for
2.2 ORGANIC SEMICONDUCTORS

Absorption
Intersystem Crossing
Fluorescence
Internal Conversion

\[ S_0 \]

\[ S_1 \]

\[ S_2 \]

\[ T_1 \]

\[ T_2 \]

\[ T_3 \]

Phosphorescence

Figure 2.6: Jablonski scheme depicting the electronic singlet and triplet states with their vibrational levels. Solid lines denote optical transitions. (Figure modified from Ref. [23].)

Commercialisation of organic photovoltaics remain demanding. Materials introduced so far share that they are all of p-type, i.e. they generally exhibit significantly higher hole than electron conductivity. Synthesising good n-type materials has for a long time been very challenging, but one of the few examples of a well-performing n-type material is N2200, based on a naphthalene diimide (A) linked to thiophene sub-units (D) as shown in Figure 2.4 right. [22]

2.2.2 Interaction with Light

The Jablonski diagram, as shown in Figure 2.6 allows to depict possible photophysical transitions in a simple way. If a system (e.g. a molecule or polymer segment) is in its ground state \( S_0 \), the electrons fill up all states beginning from the deepest. Each state will be occupied by two electrons of opposite spin (up and down) giving rise to a multiplicity of one – therefore called singlet state. The absorption of a photon occurs quasi-instantaneously and can promote the electron to a higher lying singlet state \( S_n \). Each of these singlet states includes vibrational and possibly rotational sublevels. The latter of which are omitted in Figure 2.6 for clarity. If a transition ends in a vibrationally excited state, the electron quickly (few ps) undergoes internal conversion, commonly due to non-radiative relaxation, and moves to the ground state of that
The Frank-Condon principle describes that vibronic transitions occur vertical with respect to the nuclear coordinate $R$ (a). Vibrationally excited states relax quickly into the ground state of the electronic level. Transitions thus predominantly start from this level and end in the vibrational manifold of the electronic final state and the respective spectra can be mapped in optical spectroscopy (b). Adapted from Refs. [3,24].

For two electrons with parallel spin, there is a multiplicity of three. Such states are thus called triplet states. Transitions from singlet to triplet states, i.e. inter system crossing (ISC), are spin-forbidden, but can occur due to spin-orbit coupling (especially in presence of heavy atoms). Triplet states also include vibrational sublevels as discussed for singlets. Photon emission from triplet states due to a transition back to the $S_0$ (phosphorescence) is a forbidden process as well, leading to a significantly longer lifetime of triplets (up to milliseconds). Triplet states generally lie lower in energy than singlets, which is due to a lower Coulomb repulsion between two electrons of the same spin: as stated by the Pauli principle, they cannot occupy the same state and are thus on average farther apart from each other than electrons in singlet configuration (exchange interaction).

The probability for vibronic (vibrational and electronic) transitions can be determined by the Frank-Condon principle as explained in Figure 2.7 (a). Since the excitation into the $S_1$ state is accompanied by a change in arrangement of the electrons, this also leads to a change in nuclei conformation (here described as a changed nuclear coordinate $R$). The non-harmonic oscillators of the excited singlet states do thus not exhibit the same nuclear coordinate as their ground state ($R_0 \neq R'$). The curve corresponding to $S_1$ is usually located at a larger nuclear coordinate,
Figure 2.8: Depiction of a Wannier-Mott and a Frenkel exciton (a), showing that the latter are strongly localised due to the Coulomb attraction. Dependence of Coulomb and Bohr-radius on the permittivity for a typical organic and inorganic value (b). Adapted from Ref [25]. The Bohr radius in inorganic semiconductors significantly exceeds the Coulomb radius, leading to the formation of free charge carriers.

since electronically excited states tend to have more anti-bonding character than ground states (consider section 2.2.1). The transitions are much faster than the nuclear motion and thus run vertically with respect to \( R \) (Born-Oppenheimer approximation). While doing so, they cut through several vibrational levels, to which a transition is possible. The highest probability is found for the greatest overlap of the initial and final vibrational wavefunction \(|\langle \nu_f | \nu_i \rangle|^2\), which leads to an intensity profile for absorption and emission as illustrated in Figure 2.7 (b). The sub-peaks superimposed on the broad bands in absorption and emission hence map the vibrational structure of the \( S_1 \) and \( S_0 \) state. Often, the 0-0 transition is not observable and the separation between the first maximum of the two spectra is termed Stokes-shift.

2.2.3 Excited States in Organic Solids

Inorganic semiconductors, such as silicon or germanium, are also based on atoms with hybridised orbitals. In marked contrast, however, the interacting species forming organic solids are the polymers or molecules, bound together by van der Waals forces, instead of atomic bonds. Covalent bonds between silicon atoms, for example, are much stronger than these temporary dipole-interactions, which is why these types of solids exhibit marked differences, e.g. in their toughness, melting temperature or degree of order. Moreover, the permittivity \( \epsilon_r \) of organic films lies between two and four, whereas for inorganic semiconductors it is significantly higher (\( \epsilon_r(\text{Si}) \approx 11.7, \epsilon_r(\text{PbS}) \approx 18 \)). Due to this low permittivity, phenomena become dominant in organic materials, which have a negligible impact in classical inorganic semiconductors.

One major characteristic of organic solids is the formation of strongly bound, so-called Frenkel excitons. Electronic excitation leads to the promotion of an electron from the HOMO to the
2.2 ORGANIC SEMICONDUCTORS

Electronic polarisation

Deformation

Figure 2.9: Schematics of the effects leading to polaron formation in organic solids. A charge depicted on the central molecule creates dipoles in its environment, thus inducing an electronic polarisation. This successively also leads to a deformation of the charge carrier’s environment.

LUMO, leaving a vacancy or hole in the former and forming an electron-hole pair. Excitons are quasi-particles that describe electron-hole pairs which are not yet dissociated into free charge carriers, but still interact with each other through mutual Coulomb attraction. Their attraction leads to an exciton radius of about 1 nm and a binding energy $E_{\text{bin}}^X$ of around 0.4 eV in organic solids, which needs to be overcome in order to form free charge carriers. Excitons are also formed in inorganic solids, but the larger permittivity in these materials leads to a stronger shielding of the Coulomb attraction, thus to a significantly lower binding energy and larger size (Figure 2.8 (a)). Such weakly bound excitons are described as Wannier-Mott excitons and the typical distance between the electron and hole is an order of magnitude larger than the lattice constant.

This difference may be better understood with the example given in Figure 2.8 (b). A covalent solid with a high permittivity ($\varepsilon_r = 15$) and a typical value for an organic solid ($\varepsilon_r = 3$) are assumed, and the exciton wavefunction is approximated with the Bohr radius $r_B$ according to equation 2.1. The Coulomb radius $r_C$ is found at the distance, for which the Coulomb potential is equal to the thermal energy $k_B T$, thereby illustrating that in the latter case thermal energy is sufficient to split excitons. Both, exciton dissociation into free carriers and exciton motion, will be treated further below. First, however, the nature of charge carriers in organic solids will be discussed more closely.

Similar to excitons, also the properties of electrons and holes are affected by the low permittivity and softness of organic materials. The dominant difference, as opposed to classical inorganic semiconductors, besides the commonly encountered absence of band transport, is the formation of polarons, i.e. charge carriers surrounded by a cloud of polarised environment. Adding or removing a charge, for example to/from a polymer segment, leads to three distinct mechanisms of stabilisation. Firstly, the change in the intra-chain (or intra-molecular) electron configuration in the $\pi$-system also affects the electron distribution in the $\sigma$-orbitals, thus leading to a bond.
length alteration. The energy associated with this process is known as the geometric- or on-site relaxation energy, sometimes denoted as $\lambda$. Secondly, and more important, the electric charge leads to an electronic polarisation of its environment (Figure 2.9 top), which in return also deforms the material in the vicinity of the charge (bottom).

Although polarons have been studied intensively in organic semiconductors, uncertainties remain in fundamental aspects of their nature. The energetic position of negative and positive polarons is often discussed as being shifted into the fundamental band gap of the polymer. This shift is assumed to be due to the aforementioned relaxation of the environment that stabilises the charge carrier. As depicted in Figure 2.10 (a), the removal of an electron from an uncharged polymer to form a positive polaron was for a long time assumed to lead to the formation of two new levels in the band gap. Of these the lower one is semi-occupied due to the removal of the electron and the upper completely empty and due to a down-shift of the previously unperturbed LUMO. The analogous process for an electron addition and a negative polaron is depicted alongside the former and also exhibits two levels within the fundamental band gap – the lower fully occupied and the upper semi-occupied. This discussion is originally based on the Su-Schrieffer-Heeger (SSH) model, and has some descriptive power, but is significantly limited by the neglect of many body effects.

Despite its crude simplifications and objections from experiments, this model is the most commonly employed explanation for the optical transitions of polarons in conjugated polymers. For partially crystalline polymers with high order, it was also extended to allow for the description of polarons delocalised over several adjoining chains (inter-chain polarons), giving rise to transitions as depicted on the right hand side of Figure 2.10 (a).

Nevertheless, the model fails to account for a key observation, which is that it falsely predicts the energy needed for the addition (removal) of a second charge carrier, i.e. the second electron affinity (EA) (ionisation potential, IP) of the neutral polymer, to be larger (smaller) than the first one. Intuitively, this should not be the case, for if an additional electron really were to be localised on a polymer chain, the addition of yet another electron to this chain segment would have to overcome the Coulomb repulsion of these two carriers, which reduces the EA. Experimentally, this was observed for organic materials via XPS spectroscopy and led to the formulation of an alternative scheme of energy positions as depicted in Figure 2.10 (b). It is important to note that the relevant transport levels of electrons and holes remain shifted into the fundamental gap of the unperturbed material, but the actual occupation changes – also the position depending on the charge carrier spin.

In both pictures, the polaron formation leads to two optically active transitions below the band gap energy. The low energy transition, often termed $P_1$, is commonly found in the mid infrared spectral region between 0.3 and 0.5 eV and the higher energy transition ($P_2$) is located slightly below the band gap energy of the unperturbed polymer. These features will be studied experimentally in Chapters 4, 5, and 6.

The order of polymer chains in films can vary significantly. Amorphous materials are fully dis-
ordered with neither an extended conjugation of the $\pi$-system in chain direction (intra-chain) nor overlapping $\pi$-systems in inter-chain direction. Highly ordered phases, however, are generally considered to be beneficial for the transport of charges and excitons (vide infra), since the strong $\pi-\pi$-interaction facilitates the transition between adjacent chains. An increased degree of crystallinity is thus often desired for manufactured devices and was one of the key aspects for an improving power conversion efficiency in OPV. Specifically, it was observed that in P3HT an increased head-to-tail ratio of the hexyl-chain leads to a significant improvement of the crystallinity from a completely amorphous film in case of regio-random P3HT to a high degree of crystalline domains for the regio-regular variant.\[34\] Besides a better planarisation of the chain, i.e. more extended $\pi$-system in the chain direction, the regular alignment of the tail also leads to an improved overlap of the $\pi$-systems, i.e. delocalisation over adjacent chains.\[35\] A strong interaction of adjoining $\pi$-systems commonly leads to a higher carrier mobility in inter-chain direction than along the polymer backbone, where kinks and torsion tend to hamper the free movement of charge carriers between conjugated segments.

The strong inter-chain interaction can often be observed by a red-shift in the absorption onset for a higher regio-regularity. The intermolecular coupling furthermore leads to the formation of a pronounced vibrational structure in the absorption spectrum.\[36,37\] Agglomeration of polymer chains can additionally generate so-called J- or H-aggregates. The optical properties in these confirmations can significantly vary with respect to those of isolated chains, e.g. in solution.\[38,39\]

Further strategies to increase the film crystallinity of polymer films include an increased molecular weight (longer chains are able to fold back into themselves and thereby increase the order), slow film drying by using slowly evaporating solvents or saturated atmospheres,\[41\] thermal annealing above the polymer glass temperature or the mixing with high-boiling

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**Figure 2.10:** Polaron energy levels and occupation with respect to the fundamental band gap according to the classical representation based on the SSH model (a) and as recently proposed by Heimel (b).\[33\] Blue arrows indicate the optically allowed transitions accessible in doping- or photoinduced absorption spectroscopy.
additives in order to induce a de-mixing in blends. \[44,45\]

Figure 2.11 gives an overview of effects in organic solids as discussed so far. The energies are defined relative to vacuum, which is set to zero. The left hand side displays the energy levels for an isolated chromophore. \[23\] The states are occupied up to the HOMO, which lies at a position corresponding to the ionisation potential. This ionisation potential is the energy required to remove one electron from the material. Similarly, the energy gained by adding an extra electron to the molecule is termed the electron affinity and describes the difference between the vacuum energy and the LUMO. The difference between IP and EA is the band gap in gas phase $E_{gas}$. For an ordered or crystalline organic solid, as depicted in the centre, the valence and conduction level shift closer together, giving rise to the transport gap $E_{trans}$. In other words, the EA is increased and IP is reduced by the polarisation energies $P_e/P_h$ respectively. This is the stabilising energy leading to the formation of polarons instead of free charge carriers discussed above. Additionally, in contrast to the discrete states of single molecules in gas phase, crystalline solids exhibit a broadening of the valence and conduction state due to the formation of electronic bands. The right hand side, finally, depicts the case for a material in presence of disorder. The states are commonly assumed to exhibit a Gaussian distribution leading to a broadening of electronic states that is not due to their superposition. In the two solid cases, the energy difference between the valence and conduction level is termed the transport gap, because this is the energy separation of the transport levels of electrons and holes (or the polarons, to be precise). In order to understand the optical processes, the states introduced in the Jablonski diagram (Figure 2.6) have been included on the right hand side in Figure 2.11. Note that these two concepts are not compatible. The molecular energy levels are defined with respect to vacuum and in the Jablonski scheme everything is scaled relative to the ground state $S_0$. $S_0$ is here aligned with the
HOMO level to illustrate the connection of the exciton binding energy $E_{bin}$, which is given by the energy difference between the $S_0 \rightarrow S_1$ transition (optical band gap $E_{opt}$), and the transport gap $E_{trans}$.

2.2.4 Carrier Transport in Disordered Systems

Once excitons or polarons are generated in organic solids, these particles can move through the film and recombine via different mechanisms or can be extracted at external contacts. The following section is devoted to discussing the concepts of transport, which, in large parts, are also applicable for the material classes discussed farther below.

Exciton migration can occur trivially due to the emission and re-absorption of photons, but more typical for solids is non-radiative diffusion. In disordered materials, this process occurs as incoherent hopping from one conjugated $\pi$-segment to the next. The classical descriptions are through a Förster-like process or through Dexter transfer. The former, also known as fluorescence resonance energy transfer (FRET), is a resonant process between an emitter (the initial segment) and a receiver and can occur if the emission spectrum of the former overlaps with the absorption spectrum of the latter and if their dipole moments are non-orthogonal (Figure 2.12 (a) top). This resonant process involves the exchange of a virtual photon and can occur over a certain distance; its efficiency typically decreases with $r^{-6}$. An efficient interaction is commonly observed for distances between 2 and 5 nm. Since the FRET conserves the spin of both the emitter and receiver, only singlet excitons can be transferred with this mechanism. Notably, the FRET was initially formulated for diluted solutions of point-like chromophores – an approximation, which might not hold in solid films of chromophores with extended conjugation. Nevertheless, FRET offers a good qualitative understanding of transport through receiver-emitter systems.

Dexter transfer describes the double exchange of electrons due to the wavefunction overlap of adjacent sites. Given the necessary overlap, it is limited to short distances (approx. 1 nm) and its efficiency decreases exponentially with site separation. It can be thought of as a simultaneous exchange of one electron from the LUMO of the emitter to the LUMO of the receiver and a back transfer of an electron from the HOMO of the receiver (Figure 2.12 (a) middle and bottom). This process also allows for the migration of triplets as long as the overall spin is conserved. Similar to the Förster process, though, it is favoured when the exciton energy of the emitter is larger than that of the receiver.

Figure 2.12 (b) summarises the processes an exciton may undergo in its lifetime. During the random migration due to hopping, it possesses a finite probability to eventually recombine (germinately) either non-radiatively through thermalisation or radiatively through the emission of a photon. Furthermore, excitons might dissociate into free charge carriers, for example in the

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presence of an energy offset for the HOMO/LUMO levels of adjacent sites. The average distance travelled by an exciton is the diffusion length $L_D$, which is an especially critical parameter in solar cells, and commonly lies below 20 nm.

As illustrated in Figure 2.13, all excitations would undergo a rapid downhill migration to sites with the lowest energy, when at zero Kelvin (observable as red-shifts in PL). In presence of finite temperature, however, excitons are also able to carry out small up-hill jumps in energy and therefore move iso-energetically on a dynamic equilibrium transport level after the initial fast down-hill migration. The density of exciton states is typically assumed as a Gaussian distribution with a width of 50-110 meV.

Once free charge carriers are formed, they can also move through random diffusion analogously...
to excitons or, when in presence of an electric field, through drift. Although these carriers can be delocalised over the π-systems of polymer segments, their transport does not occur through Bloch oscillations. In most cases, a phonon mediated hopping between polymer sites is observed, a concept initially introduced for impurity mediated conduction in inorganic materials (thus neglecting polaronic effects). For the hopping rate $v$ from a site $i$ to a site $j$, the Miller-Abrahams formalism is often employed, which distinguishes between hopping events with a gain or a loss in energy:

$$v_{ij}^{\text{Miller}}(\Delta E_{ij}, r_{ij}) = v_0 \exp \left[ -2\gamma_r r_{ij} - \frac{\Delta E_{ij} + |\Delta E_{ij}|}{k_B T} \right].$$

(2.3)

Here, $v_0$ is the maximum hopping rate and $r$ is the spatial- and $\Delta E$ is the energetic separation respectively. The first exponential term describes the wavefunction overlap between adjoining sites via the inter-site distance and the inverse localisation radius $\gamma_r$. The second term determines whether the process is thermally assisted in case of upwards jumps.

This Miller-Abrahams formalism is a simplified version of the Marcus rate. The latter is commonly used to describe electron transfer reactions in chemistry and – crucial for organic solids – also accounts for polaronic effects. For the hopping rate one finds

$$v_{ij}^{\text{Marcus}} = \frac{I_{ij}^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp \left[ -\frac{(\Delta G + \lambda)^2}{4\lambda k_B T} \right],$$

(2.4)

with the reorganisation energy $\lambda$, Gibbs free energy $\Delta G$ (which includes the energy difference $\Delta E_{ij}$ from equation 2.3) and the overlap integral $I_{ij}$ between the sites. The Marcus expression assumes the initial and final site to be located in a potential well separated by an energy barrier corresponding to the reorganisation energy $\lambda$. This mimics the polaronic nature of charge carriers in organic solids. Both approaches mentioned are semi-classical and break down for $T \rightarrow 0$. Alternatively, quantum mechanical descriptions such as nuclear tunnelling are able to describe transport at that limit, but reduce to the semi-classical Marcus expression for the experimentally relevant temperatures.

Analogous to the discussion for exciton migration above, the site-disorder is commonly modelled as a Gaussian distribution:

$$g(E) = \frac{N_t}{\sqrt{2\pi}\sigma^2} \exp \left[ -\frac{(E - E_0)^2}{2\sigma^2} \right],$$

(2.5)

where $E_0$ is the centre of the DOS, $N_t$ is the density of hopping sites and $\sigma$ is the variance in energy (diagonal disorder). Typically, the transport through polymers is assessed via the charge carrier mobility $\mu$, which characterises the drift velocity of the carrier when applying an electric field. In the so-called Bässler or Gaussian disorder model (GDM) for high electric fields, the
mobility was calculated by Monte-Carlo simulations and determined to be: \[ \mu_{GDM} = \mu_\infty \exp \left[ \frac{-2\sigma^2 k_B T}{3 k_B T} \right] \times \begin{cases} \exp \left( C \left[ (\sigma / 2 k_B T)^2 - \Sigma^2 \sqrt{F} \right] \right) & \Sigma \geq 1.5 \\ \exp \left( C \left[ (\sigma / 2 k_B T)^2 - 2.25 \right] \sqrt{F} \right) & \Sigma < 1.5, \end{cases} \] (2.6)

where \(\mu_\infty\) is the mobility in the limit of infinite temperature, \(C\) is a constant depending on the inter-site distance (typically 1-2 nm), \(\Sigma\) is the disorder in site-separation (off-diagonal disorder) and \(F\) is the magnitude of the electric field. Since the hopping is phonon assisted, the mobility increases with temperature (contrary to band transport). Moreover, also an increased electric field assists the transport.

An additional aspect, which is neglected in the GDM, is the dependence on the charge carrier density. As evident from the sketch in Figure 2.13, an increased carrier density leads to the filling of the DOS from the bottom, for which hopping events are less likely than in the middle of the DOS. The mobility thus increases with the carrier density. Since the carrier density is also affected by the temperature, the observed trend of the mobility typically follows an Arrhenius-like behaviour instead of \(\ln(\mu) \propto T^{-2}\), as predicted by Bässler. The GDM furthermore assumes the energy of adjacent sites to be uncorrelated, which is not necessarily true.

A result of this model is that, similar to excitons, carriers brought into the DOS rapidly thermalise (as shown in Figure 2.13) and reach an equilibrium transport energy, which lies \(\frac{\sigma^2 k_B T}{k_B}\) below the DOS maximum. Charge carriers might also (non-geminately) recombine when encountering free carriers of opposite sign (bimolecular recombination) or mediated by trap states (Shockley-Read-Hall recombination).

### 2.2.5 Charge Generation

Charge photogeneration in organic solids is most commonly discussed in the context of organic photovoltaics. Although this thesis does not focus on OPV itself, it is helpful to briefly discuss the underlying ideas of the community. As detailed above, the small permittivity of organic solids is commonly expected to not allow for prompt charge formation upon photon absorption, but expected to create strongly bound Frenkel excitons. In order to effectively dissociate excitons, materials are blended together to create what is termed a bulk heterojunction. Historically, this was most commonly carried out by using a strongly absorbing polymer as electron donor and a fullerene derivative (PCBM) as acceptor material. Quite recently, also non-fullerene acceptors attracted much attention with well superior performance than in classical systems. In the simplest picture, as depicted in Figure 2.12 (b) on the right, the energy offset between the respective HOMO and LUMO level of acceptor and donor are assumed to promote the exciton dissociation.

In more refined discussions, a charge transfer state (CTS) is often invoked to explain the dissociation in more detail. As depicted in Figure 2.14 this intermediate state forms at the interface
between two phases and was observed experimentally in many different blends for example via high sensitivity absorption, photo- and electroluminescence, or photocurrent spectroscopy.\cite{69-72}

Nonetheless, there is still an intense debate about the precise mechanism and different impacts on the exciton dissociation. For example, it was observed that charge formation may also occur quasi-instantaneously during several tens of fs,\cite{73} which is in contrast to exciton diffusion towards an interface, as this process would require several ps.\cite{74} It was thus proposed that additionally to the neat donor and acceptor phases, blended materials also form finely intermixed regions, wherein a significant exciton population is generated directly at an interface.\cite{75} A detailed discussion of charge generation at donor-acceptor interfaces and the role of the CTS may be found in the reviews included in the bibliography.\cite{76-78}

Nevertheless, photogeneration of charges is generally also observed in neat polymers, albeit with a significantly lower yield. Sources of charge generation are chain defects, such as kinks, which lead to an energetic driving force for exciton dissociation.\cite{79} Similarly, the mixture of crystalline and amorphous regions within a polymer film can create internal homojunctions, at which driving forces can be present as well.\cite{80,81}

Charge formation is again also observed at ultrafast timescales.\cite{82,83} While there is still room for debate on the precise mechanism, several reports indicate that excitons, when formed, are initially delocalised over a large part of the polymer backbone (up to 9 nm after 100 fs were reported\cite{84}) and then quickly localise or self-trap.\cite{85,86} It was argued that this process occurred as coherent energy transfer through a series of delocalised states\cite{57,48,7} and that dissociation was the result of incomplete tunnelling.

For donor-acceptor polymers, the initially formed excitons were furthermore reported to already exhibit a partial charge transfer character, which might be a precursor for exciton dissociation.\cite{13,14,88} Fittingly, the polaron yield in these materials is often observed to be significantly larger than for homopolymers.
2.3 Carbon Nanotubes

2.3.1 Opto-electronic properties

Carbon nanotubes (CNTs) can conceptually be considered as a sheet of graphene, i.e. a honeycomb layer of $sp^2$-hybridised carbon, rolled-up into a hollow cylinder. The hexagonal lattice of graphene with its unit vectors $\vec{a}_1, \vec{a}_2$ and the translational indices $(n, m)$ is then used to describe the so-called chirality of the nanotube (Figure 2.15(a)). A carbon atom in the virtual rolling-up process will be projected onto another atom on the circumference, $[89]$ This projection can be described using a vector

$$\vec{C} = n\vec{a}_1 + m\vec{a}_2; n \geq m,$$  \hspace{1cm} (2.7)

which points perpendicularly to the tube axis. This translation forms an angle $\theta$ between $\vec{a}_1$ and $\vec{C}$, which may lie between 0 and 30° and comprises all possible chiralities due to the six-fold rotational symmetry of the graphene lattice. For the two extreme cases, the tubes are strictly speaking not chiral and for $\theta = 0^\circ$ one finds $n = 0$ and for $\theta = 30^\circ$ $n = m$. The former are referred to as zigzag- and the latter as armchair tubes due to the shape of the CC-bonds limiting these tubes (examples are given in Figure 2.15(b)). The chiral angle can be determined using

$$\cos \theta = \sin^{-1}\left(\frac{\sqrt{3}m}{2\sqrt{n^2 + nm + m^2}}\right).$$  \hspace{1cm} (2.8)

It is furthermore possible to directly determine the circumference $|\vec{C}|$ and diameter $d_t$ of a CNT from the chiral indices $(n, m)$ using

$$|\vec{C}| = a_0 \sqrt{n^2 + nm + m^2}$$  \hspace{1cm} (2.9)

and

$$d_t = \frac{|\vec{C}|}{\pi} = \frac{a_0}{\pi} \sqrt{n^2 + nm + m^2},$$  \hspace{1cm} (2.10)

where $a_0$ is the graphene lattice constant, connected to the distance between two carbon atoms $a_{CC}$ as $a_0 = \sqrt{3}a_{CC} = 0.246$ nm.

Commonly, CNTs of different chirality and with a number of walls are formed during synthesis. While multi walled CNTs (MWCNTs) can form, they are generally not employed in electronic applications. The following discussion thus solely focuses on single walled CNTs (SWCNTs).\textsuperscript{1} CNTs are marked by their large aspect ratio, leading them to be virtually one-dimensional materials. In their axis direction, CNTs can be as long as several centimetres and with a diameter range between 0.5 and 3 nm, their circumference gives rise to a strong confinement in off-axis direction.

\textsuperscript{1}Unless stated otherwise, the term CNT will be used in this thesis to refer to SWCNTs to maximise the readability.
When describing the electronic properties of SWCNTs, it is again useful to consider the graphene lattice (zone folding approach) as depicted in Figure 2.16 (a). The corresponding reciprocal lattice, shown in (b), is defined by the vectors $b_1$ and $b_2$ and the first Brillouin zone (blue shaded region) includes the characteristic points $\Gamma$, $K$ and $M$. The relevant point for optical transitions is the $K$-point, at which the valence and conduction band meet and exhibit a linear dispersion – so-called Dirac cones – as displayed in (c).

Given the extended nature of CNTs in axis direction, the wave vector component parallel to the tube $\vec{k}_\parallel$ is continuous and follows the dispersion of graphene. In circumferential direction, however, the wave vector $\vec{k}_\perp$ obeys periodic boundary conditions, giving rise to quantised values $\vec{C} \cdot \vec{k}_\perp = 2\pi j$, where $j$ is a non-zero integer. This set of vectors is indicated as parallel lines in Figure 2.16 (c) and their projection onto the graphene band dispersion determines the allowed states in CNTs. If the parallel lines cut through the Fermi point $K$ or $K'$, the resulting tubes exhibit a finite DOS at the Fermi level, thus behave like a metal. In all other cases, a band gap forms and the tubes behave like semiconductors. Since this dependence is solely governed by the tube chirality, the indices $(n, m)$ can be used to determine the CNT electronic character as follows:

$$ (n-m)\text{mod}3 = \begin{cases} 
0: \text{metallic} \\
\text{else: semiconducting} 
\end{cases} $$

Statistically, a third of CNTs is hence metallic and two thirds are semiconducting (indicated by coloured circles in Figure 2.15 (a)). Consequently, all armchair tubes are metallic. To be precise, if curvature effects are taken into account (which are neglected in the zone folding approximation), a small secondary band gap opens for non-armchair tubes and scales inversely with the tube diameter. [92,93]

As illustrated in Figure 2.17 (a), the DOS of both species is marked by van Hove singularities,
typical for one-dimensional materials (Figure 2.1). The electronic transitions between these singularities are denoted $S_{ij}$ and $M_{ij}$ respectively. Only transitions with $i=j$ are allowed for light polarised longitudinally to the tube axis. At a comparable size, the $M_{11}$ transition lies at a higher energy than the $S_{11}$ and $S_{22}$ transitions, as depicted in the Kataura plot in Figure 2.17 (b). The transition energy $E_{ij}$ roughly scales proportional to the inverse diameter $d_t$. Deviations, which are more dominant for smaller diameters, are due to the impact of the chiral angle called the curvature and trigonal warping effect. This leads to the formation of so-called family patterns for the optical transitions when grouping them according to their chiral angle.

For light polarised transversal to the axis, $i = j$ transitions are suppressed, but $S_{12}$ or $S_{21}$ transitions are allowed (Figure 2.18 (a)). Due to the antenna effect, the cross section for this polarisation is significantly lower, making CNT absorption spectra strongly dominated by longitudinal excitation.

Based on the initial free electron calculations of the CNT DOS, the narrow peaks observed in the absorption and emission spectra of CNTs (vide infra) were attributed to direct transitions of free carriers between the VHSs. Soon, though, it was observed that this model failed to account for experimental observations (ratio problem). More refined calculations, taking many-body effects into account, showed that optical transitions in CNTs are due to strongly bound excitons, at least for the lower lying transitions. The strongest experimental evidence was found in two-photon absorption experiments or the analysis of exciton-phonon side bands. The exciton binding energy is size dependent and of the order of 0.4 eV, thus comparable to the one found in disordered organic solids (section 2.2.3). The exciton size was initially determined to be around 2 nm, but a more recent study suggests a size of 13 nm.

**Figure 2.16:** Direct (a) and reciprocal (b) lattice of graphene. The band around the K- and K’-point is marked by the linear dispersion of a Dirac cone (c). In CNTs, the k-vector perpendicular to the axis is quantised, giving rise to parallel lines of allowed states in k-space. Their projection onto the Dirac cone defines the CNT band dispersion.
Figure 2.17: The DOS of metallic and semiconducting CNTs is marked by narrow van Hove singularities (a). The transition energies as a function of the tube diameter can be summarised in the so-called Kataura plot (b). 

Figure 2.18: The optically allowed transitions in CNTs depend on the polarisation (a) of incoming light. The valley degeneracy shown in (b) leads to the splitting into four excitonic states, of which only one direct transition is bright (c). The lowest lying state is dark. Adapted from Ref. [107].

The valley degeneracy of the $K$ and $K'$ points in momentum space (where optical transitions occur) leads to a splitting into four different electron configurations for singlet excitons. Two of these ($KK$ and $K'K'$) are direct and the other two ($KK'$, $K'K'$; K-momentum dark exciton) are indirect excitons (Figure 2.18 (b)). The same effect leads to twelve degenerate triplet excitons. The bonding and antibonding combinations of the two direct exciton wavefunctions and short-range Coulomb interactions lead to a splitting of these levels with different effective masses (as indicated by the different curvature in (c)). Only the upper direct exciton is a so-called bright state and the lowest lying state is a dark exciton. Their valleys are separated by a few meV, which is often invoked as an explanation for the low PL quantum yield. Crucially, the existence of this dark exciton was experimentally verified by its brightening induced by the Aharonov-Bohm effect in a magnetic field. 

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In absence of such a magnetic field, PL generally arises from the $S_{11}$ bright exciton. The quantum yield (QY) for this process typically lies below 1%.\cite{115,116} Transient spectroscopy studies furthermore reveal short exciton lifetimes of up to 100 ps,\cite{117} which is significantly lower than the theoretically predicted 100 ns.\cite{115} This discrepancy is often attributed to the above mentioned dark exciton quenching, but also strongly dependent on the CNT environment and exciton quenching through defects or interactions in CNT bundles.\cite{95,118} Similarly, also the transition energy (via the exciton binding energy) is strongly affected by the environment, and individually suspended tubes in air or vacuum typically show a blue shift compared to tubes in a dielectric medium.\cite{119,120} Exciton quenching is furthermore enhanced by defects, for example at the ends of the tubes as observed by lower PL emission towards the edges.\cite{121}

The motion of excitons through networks of CNTs occurs via diffusion (consider section 2.2.3) and also greatly depends on the environment. CNTs wrapped with PFO, for example (vide infra), exhibit a diffusion coefficient significantly larger than that found when surfactants surround them. An even higher value was observed for clean air-suspended tubes, which is consistent with the assumption that exciton diffusion is not only affected by intrinsic phonons, but also potential fluctuations or extrinsic phonons.\cite{116,122} For further reading on excitonic behaviour in CNTs also consider the reviews by Dresselhaus or Miyauchi.\cite{107,123}

So far, the focus of the discussion lay on the singlet exciton. Besides triplet excitons, also higher order many particle states have been observed in CNTs.

Triplets were reported to be responsible for a strong delayed fluorescence in CNTs\cite{124} and allegedly observed in transient absorption spectroscopy.\cite{125} In the latter case, however, the overwhelming evidence in literature points to a different assignment of the observed feature, namely to be due to trions. A trion is a quasi-particle comprising either two electrons and one hole or vice versa (consider Figure 2.19). Due to the exchange interaction and trion binding energy, these states form approximately 100-200 meV below the bright singlet state\cite{125,126} and were
be observed \textit{via} absorption, photo- and electroluminescence or ultrafast transient absorption spectroscopy. \cite{127,131}

For ultrafast experiments, the formation of biexcitons was furthermore reported. \cite{129,132} Biexcitons are a four-particle state involving two electrons and two holes, which was predicted to exhibit a binding energy of about 100 meV. \cite{133} Despite the large exciton binding energy, also the generation of long-lived charges is generally observed in CNTs, similar to the neat polymers. \cite{134,135}

\subsection*{2.3.2 Single Walled Carbon Nanotube Spectroscopy}

Absorption spectra of SWCNTs commonly exhibit the first two transitions of semiconducting tubes in the NIR and red region of the spectrum (for tubes with a diameter of around 1 nm). Metallic tubes are commonly found in the visible range between the $S_{22}$ and $S_{33}$ transitions. Bundled tubes exhibit broadened absorption peaks as opposed to the sharp peaks found for tubes individualised, \textit{e.g.} \textit{via} polymer wrapping. Absorption spectroscopy can thus be used as a reliable tool to assess the material quality. CNTs are reported to exhibit a high oscillator strength, with a cross section of up to $10^{-17}$ cm$^2$ per C-atom for the $S_{22}$ transition of (6,5) tubes.

Figure 2.20 (a) depicts the absorption spectrum of a polychiral sample, where more than just one absorption peak appears in the indicated spectral region. The first and second semiconducting transitions are distinctively visible. No peaks of metallic tubes are observable, which points to the high purity of polymer wrapped CNTs. As discussed above, optical transitions in CNTs are predominantly due to longitudinal excitons, but transverse excitons can also exhibit a small absorption, which can be used to access important information about the band structure and electron-hole symmetry. \cite{136,137} Additional to the main peaks, absorbance spectra also often exhibit a background signal, which increases towards higher energy. This can be due to scattering and graphitic residues in case of samples of low quality or due to the interaction with $\pi$-plasmons. Moreover, close inspection of the region of the first semiconducting transitions reveals additional smaller features approximately 200 meV above each excitonic peak. These are due to the promotion of an electron into the indirect dark exciton, which occurs, when a photon interacts with zone-boundary (K-momentum) phonons. \cite{138}

CNT photoluminescence, as discussed above, generally stems from the bright $S_{11}$ exciton. Commonly, individualised tubes give rise to significantly brighter PL than bundled tubes, which exhibit additional rapid non-radiative decay channels. PL excitation spectra (or action spectra) typically show a strong signal for direct excitation of the $S_{ii}$ transitions, as expected from the absorption spectra discussed above. Plotting the PL emission energy as a function of the excitation energy gives rise to a two-dimensional map, \cite{139} which is often used to analyse the different chiralities present in a sample. As shown in Figure 2.20 (b), the PLE map is marked by several bright spots, which are arranged horizontally and mark the $S_{11}$ emission.
Similar to the discussion of the absorption above, weak side bands, approximately 140 meV below the main peaks can be observed. These peaks can again be understood as K-phonon mediated emission from the indirect dark exciton. Assuming this state to lie 30-40 meV above the bright direct exciton (Figure 2.18) and with a K-momentum phonon energy of 170 meV (1580 cm$^{-1}$), this corresponds to an absorption observable 200 meV higher in energy than the main peaks and a PL 140 meV lower than the main peaks, [140,141] Also consider Ref. [107] for a more detailed explanation.

A major part of CNT analysis has been carried out via Raman spectroscopy. Although this technique will not be applied in this thesis, the findings are relevant for the understanding of the observed vibrations in the mid infrared spectral region. A good introduction can be found in the thorough review papers by Dresselhaus, [142,143] Similar to the discussions above, the phonon modes of CNTs can be best understood when considering the graphene Brillouin zone. Graphene contains two atoms in its unit cell, thus giving rise to six phonon branches. A virtual rolling up of the sheet, analogously to the electronic spectra, leads to the phonon spectra of CNTs.

The most important modes are the G-band, radial breathing mode (RBM) and D or G$^*$ mode. The G-band spectra, which are split into many features around 1580 cm$^{-1}$, and the lower frequency radial breathing mode (RBM), are usually the strongest features in SWNT Raman spectra. The former is common to all $sp^2$-carbon forms and due to stretch vibrations of C-C bonds. While there is just one G-band observable in graphene, up to six G-band phonons can be allowed in chiral CNTs due to the curvature of the tubes. Typically, though, only two of them are experimentally observed. The G$^*$ mode is due to longitudinal optical phonons and is typically found at 1582 cm$^{-1}$ as well and hardly affected by the chirality and size. The G$^-$ mode, however, which is due to an in-plane transverse optical phonon, is strongly dependent on the tube diameter and
shifts towards lower frequency for smaller diameters. Besides being a good probe for the diameter, the G$^-$ band is also sensitive to whether the tubes are metallic or semiconducting. In semiconducting tubes, it exhibits a Lorentzian line shape, just as the G$^+$ mode does in either case, but for metallic tubes, a broad Breit-Wigner-Fano lineshape was observed and attributed to a Kohn anomaly.

In contrast to the G-mode, the RBM is a vibration unique to CNTs, which arises from their tubular structure. It can be described as a simultaneous out-of-plane movement of the atoms perpendicular to the tube axis and is thus highly sensitive to the tube diameter. Generally, it is found in the region from 100 to 500 cm$^{-1}$. The frequency of this vibration $\omega_{RBM}$ can be calculated as

$$\omega_{RBM} = \frac{227}{d_t} \sqrt{1 + C_e d_t^2},$$

where $d_t$ is the tube diameter and $C_e$ accounts for the tube environment (often $C_e \approx 248$ cm$^{-1}$).

The D-band, finally, which lies between 1300 and 1400 cm$^{-1}$, is due to disorder-induced second-order Raman scattering, as known from graphite and graphene. Uncharacteristically, it shifts with the excitation energy (dispersive behaviour). For perfect, i.e. defect-free CNTs, however, it should be absent. It is thus a good indicator for the material quality and purity.

Similarly, also the 2D (alternatively D$^*$ or G') band, located around 2700 cm$^{-1}$, is due to a second-order Raman process and is considered as an overtone of the D-band. In contrast, though, it does not require disorder to be present.

### 2.3.3 Sorting and Selecting Carbon Nanotubes

Although an appropriate setting of reaction conditions allows to increase the amount of semiconducting species from the statistically expected 2/3, the typical content of metallic tubes is still too high for semiconductor applications. Moreover, due to relatively strong van der Waals forces, CNTs tend to form bundles, which can corrupt their properties and makes their handling more difficult. Several techniques have been invented to sort out and de-bundle semiconducting SWCNT and increase the purity of CNT samples after synthesis. In a first step, these techniques generally rely on the functionalisation of the CNT wall to bring them into a dispersion. While initial protocols successfully brought metallic SWCNTs into water dispersion, these techniques exploited covalent reactions that break the carbon bonds of the tubes. Such side-wall reactions can change the CNT properties significantly, which is undesired. Non-covalent reactions, leaving the carbon bonds unaltered, are thus preferred.

A common way for doing so is to disperse SWCNTs in solution by use of surfactants. In water, for example, several bile salts with hydrophobic tails that orient towards the tube walls and hydrophilic head groups directed towards the solvent, were successfully used to retain CNTs dispersed in the solvent. Since these surfactants are insensitive to the CNT electronic properties, a second step has to be carried out to select only semiconducting species. The first successful
2.3 CARBON NANOTUBES

approach was via density gradient ultracentrifugation (DGU), which exploits the buoyancy difference of tubes with different diameter. A high purity of semiconducting species has been achieved with this technique by using a mixture of different surfactants.

Further techniques to sort CNTs include gel chromatography and electrophoresis. In the former, surfactant covered tubes are brought into an allyldextran-based gel and different magnitudes of van der Waals forces between the tubes and the gel lead to a columnar separation of tubes. Electrophoresis can be used with an alternating or a direct electrical field and employs the different polarisability of CNTs subjected to such a field.

Samples employed in this thesis were fabricated using the polymer wrapping technique. First introduced using single strand DNA, this technique uses the strong \( \pi-\pi \) interaction between conjugated segments of long polymer chains and CNTs. While the precise mechanism of the wrapping is still a matter of research, it is generally accepted that the polymer backbone attaches to the tube while the side chains allow for them to remain dispersed. Exposure to CNTs leads to a helical attachment of the polymer around the tubes and has the benefit that this process predominantly retains the semiconducting species in a dispersion. In a typical protocol, the CNTs and polymer are brought together into the solvent to-be and are ultrasonicated in order to break the CNT bundles. After a prolonged sonication, the dispersion is ultracentrifuged to separate the dispersed isolated tubes from undispersed bundles and metallic tubes.

The selected species depend strongly on the polymer used (selectivity) as does the yield of CNTs kept in dispersion. Polyfluorenes, for example, were shown to predominantly select tubes with large chiral angle \( \theta \) (i.e. near armchair configuration), whereas polycarbozoles can select small angle tubes.

In order to study opto-electronic phenomena in CNTs, it is often desirable to predominantly select a single chirality of CNTs, for which the polyfluorene PFO (in case of (7,5) tubes) or PFO-BPy ((6,5)-tubes) have been shown to be effective. Applications in electronic devices, however, often demand to receive a high yield and purity of semiconducting species only. Good candidates for this purpose are polythiophenes, such as P3DDT, or polyazomethines, such as PAMDD, which offers purities exceeding 99.9%. Experiments also showed that additional to the backbone, also length and branching of the side chains play a big role in determining which tubes can be selected. Especially for large diameter tubes, as found via SO synthesis, longer side chains perform favourably. Moreover, the solvent in which the wrapping is carried out strongly impacts the results. PFO, for example, exhibits a high selectivity in toluene or xylene, but loses it, when tetrahydrofuran or ortho-dichlorobenzene are used instead.
2.4 Colloidal Quantum Dots

2.4.1 Physical Properties

In the context of nano-sized objects, the terms nanoparticle (NP), nanocrystal (NC) and quantum dot (QD) are often used synonymously and although they can be used to refer to the same object, these terms focus on different aspects. The term nanoparticle most generally describes every nano-sized object, independent of its inner structure. Such objects are built up of several hundred to hundred thousand atoms, leading to a size smaller than 100 nm in every dimension. Nanocrystals are NPs with a crystalline structure. Quantum dots, finally, are a special class of NCs made of semiconducting material, for which the exciton Bohr radius (equation 2.1) is larger than the dimensions of the NC. There is thus a three-dimensional confinement acting on all carriers inside the QD and its electronic properties are strongly governed by its size (Figure 2.1). Depending on the way of their fabrication, quantum dots are in practice divided into two classes. Epitaxial quantum dots (EQD) are formed by heterostructures of the semiconductor material grown on top of a parent substrate. Colloidal quantum dots (CQDs), as used in this thesis, are synthesised via wet chemical methods. CQDs consisting of a wide range of materials have been synthesised. Most prominently Cd- or Pb chalcogenides, but also In-based semiconductors (InP, InAs or InSb), Si and Ge or recently hybrid perovskites, have been intensively investigated.

In a simplified model, the behaviour of QD energy levels can be understood by considering the "particle in a box" problem from quantum mechanics. As given from equation 2.13, the energy level separation increases when reducing the size of the box.

$$E_{n}^{\text{box}} = \frac{\hbar^{2} \pi^{2}}{2m_{e}} \left( \frac{n_{x}^{2}}{L_{x}^{2}} + \frac{n_{y}^{2}}{L_{y}^{2}} + \frac{n_{z}^{2}}{L_{z}^{2}} \right),$$  \hfill (2.13)

where $m_{e}$ is the electron mass, $L_{i}$ is the size in x,y, or z-direction and $n_{i}$ denotes the level in these dimensions. This gives rise to the size tunability of the band gap energy of the QD $E_{g}^{QD}$, as famously observed by the changing colour of CdSe CQDs of different size. This simplification, however, assumes the carriers to be in vacuum, confined by a potential barrier. In order to account for the periodic potential created by all atoms in the QD, this model can be refined. A good and intuitive approximation for the band gap energy as a function of size was given by Brus, where the confinement energy $E_{\text{conf}}$ (i.e. the increased kinetic energy of the hole and the electron in a confined space) and the Coulomb attraction between these two
2.4 COLLOIDAL QUANTUM DOTS

Figure 2.21: Absorbance spectra of PbS CQDs of different size, showing the shifting position of the first exciton peak (a). Energy gap for PbS CQDs with respect to their size using different theoretical approaches and experimental data (b) as taken from Refs. [177–182].

carriers (exciton binding energy) are added to the material’s bulk band gap $E_{g}^{\text{bulk}}$:

$$E_{g}^{\text{QD}} = E_{g}^{\text{bulk}} + E_{\text{conf}} + E_{\text{bin}}$$

$$= E_{g}^{\text{bulk}} + \frac{\hbar^2 \pi^2}{2 r^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8 e^2}{4 \pi \varepsilon_0 \varepsilon_r r},$$

(2.14)

where $r$ is the radius of the QD. The confinement term includes the effective mass $m^*$ of the hole and the electron ($h$, $e$). The Coulomb term includes the permittivity in vacuum ($\varepsilon_0$) and in the QD material ($\varepsilon_r$). Further refinements, which will not be discussed here, include effects such as the exchange interaction, shape anisotropy, internal crystal field anisotropy, band non-parabolicity and mixing of bands. [176]

When investigating a real ensemble of CQDs, there are two main differences that do not allow to observe the discrete energy levels described above. Instead, they give rise to the continuous absorption spectra as depicted in Figure 2.21(a). Firstly, due to the finite potential barriers, the confinement acts stronger on the energy levels near the bulk band edges, thus one may find discrete levels adjoining these edges whereas more distant levels still form quasi-continuous bands. [2] Secondly, when considering ensembles of CQDs, they generally possess a finite size-distribution that leads to a broadening of the observed energy levels analogous to the disorder in organic solids (section 2.2.3).

2.4.2 Lead Sulphide Colloidal Quantum Dots

PbS CQDs are amongst the most commonly fabricated and employed colloidal quantum dots. [183] This success is predominantly due to the facile synthesis of these CQDs with a relatively narrow
Table 2.1: Exciton Bohr radii of relevant semiconductors

<table>
<thead>
<tr>
<th>Materials</th>
<th>CdS</th>
<th>ZnO</th>
<th>CdSe</th>
<th>PbS</th>
<th>InAs</th>
<th>PbSe</th>
<th>InSb</th>
<th>PbTe</th>
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<td>Radius / nm</td>
<td>3</td>
<td>3</td>
<td>6</td>
<td>20</td>
<td>34</td>
<td>46</td>
<td>54</td>
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</tr>
</tbody>
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Size-distribution ≤5-10%, low trap state concentration and high reproducibility. Crucially, given the large exciton Bohr radius of about 20 nm (consider Table 2.1), NCs with a diameter of more than 10 nm already fall into the strong confinement regime. The band gap can therefore be tuned almost from the bulk value of 0.41 eV at 300 K \[171\] up to more than 2 eV (\textit{vide Figure 2.21} (b)). This allows for a broad coverage of the solar spectrum, which is one reason for the great interest in PbS CQDs for photovoltaic applications. Besides the tunability of the band gap, PbS CQDs exhibit an eight-fold degeneracy of the first excitonic transition, \textit{i.e.} a high oscillator strength, as well as a high permittivity and relatively large carrier mobilities in films (\textit{vide infra}). The additional possibility for a multi exciton generation (MEG), \textit{i.e.} a path to overcome the Shockley-Queisser efficiency limit, makes it very attractive for solar cell applications. \[184\] Since both chemical elements are abundant and low in cost, PbS is additionally a good candidate for large scale fabrication.

According to the NREL efficiency chart, the driving material behind the development of the CQD photovoltaic technology was PbS. \[187\] Solar cells were first built as simple Schottky-type devices of PbS CQDs covered with bidentate thiol ligands (section 2.4.3). These devices offered efficiencies exceeding 5%. \[188\] A next step was the observation of an efficient injection of electrons into TiO\textsubscript{2}, \[189\] allowing for better selective contacts towards the electrodes. The discovery of air stable ligands, finally, made it possible to fabricate devices with CQD-based pn-junctions, \[190\] giving rise to power conversion efficiencies exceeding 10%. \[191\] In other words, PbS CQD solar cell efficiencies are nowadays almost on a par with single junction organic solar cells.

An additional focus of research is the fabrication of field effect transistors (FET) comprising films of PbS CQDs. These devices are not only relevant for future application in thin film and flexible electronics, but are also a viable tool to characterise the charge carrier transport- and electronic properties of CQD solids. FETs have, for example, been used to assess the doping level, the trap state density or the position of the valence and conduction states. \[192\]-\[194\] PbS CQDs have furthermore been used as n-type layer in combination with p-type CNTs in a fully solution-processed thin film inverter, which is an important step towards the commercialisation of electronic devices based on this material class. \[195\]

### 2.4.3 Colloidal Quantum Dot Solids

For optoelectronic applications, CQDs commonly need to be deposited as solid films on a substrate. A broad range of techniques is available for doing so, including purely lab-scale approa-
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ches (drop-, spin- or dip-coating), but also more intricate techniques that allow for a later upscaling of device manufacturing, e.g. spray coating or inkjet printing. For many applications, the long and electrically insulating ligands covering the surface of the CQDs (forming an approx. 2 nm thick shell) need to be exchanged for shorter entities. This process brings the CQDs into closer proximity and allows charges to easily flow through the CQD network. Exchanging the ligands furthermore commonly renders the CQDs insoluble in the original solvent, offering the possibility for a layer-by-layer deposition process, often employed in order to fabricate thicker and pinhole-free films.

Photoexcitation of CQD films generates localised excitons. Due to the finite size-distribution of CQDs and variation of their local environment, the energy levels exhibit a finite distribution, leading to exciton diffusion similar as for organic materials discussed above (section 2.2.3). The exciton binding energy in these systems, however, is significantly lower than in organic solids (reported to be around 30 to 60 meV), making exciton dissociation more probable. Increasing the inter-dot coupling has been reported to assist exciton dissociation into free charge carriers via tunnelling processes. The effect of inter-particle coupling can be understood by considering the exchange coupling energy $\beta$, which is related to the probability $\Gamma$ for charge carriers to tunnel into adjoining CQDs:

$$\beta \approx \hbar \Gamma \approx \exp \left( -\frac{2m^*}{\hbar^2} \Delta E \right). \quad (2.15)$$

Here $m^*$ is the carrier’s effective mass, $\Delta x$ is the width and $\Delta E$ is the height of the inter-particle potential barrier. The exact mechanism of the exciton decay, however, depends on several morphological parameters.

When discussing CQD solids, it is useful to define different regimes depending on the strength of the inter-particle coupling and disorder as illustrated in Figure 2.22 (a). For weak coupling, the electronic structure of individual CQDs can be described as confined wavefunctions localised on each respective CQD (Figure 2.22 (b) and (c) bottom). When brought into closer proximity, shared orbitals, delocalised over a domain of several CQDs (strong coupling) start to form ((b), (c), middle). In the case of strong coupling and high order, the delocalisation might also extend throughout the entire film to form mini-bands analogous to bulk solids (bottom). Additional to the coupling energy, the electronic structure and transport properties are also affected by the Coulomb charging energy $E_C$ and the site energy disorder. The former can create a Coulomb energy gap (Hubbard gap), known as the Coulomb blockade, as depicted on the bottom right in Figure 2.22 (a), but will not be discussed here in detail.

Depending on the degree of coupling and disorder, free carriers will move in the solid via different transport mechanisms. These could include band transport, direct tunnelling without the help of phonons or phonon-assisted hopping. In most cases, low carrier mobilities are observed, which arise predominantly due to hopping through localised quantum confined
Figure 2.22: Impact of disorder, coupling $\beta$ and charging energy $E_C$ on the formation of different carrier localisation regimes (a). Scheme of CQD solids (b) and the corresponding energy levels (c) for a high degree of order (top), variation in inter-particle distance (middle) and variation in particle size (bottom).

Depending on the temperature, this motion is either described through nearest neighbour hopping (NNH) or (Efros-Shklovskii) variable range hopping ((ES)-VRH).

As expected from equation 2.15, the charge carrier mobility can be greatly affected by the inter-particle spacing $\Delta x$. The strong influence of the surface ligand covering the CQDs on the spacing was initially shown for PbSe, for which the conductivity of a film could be increased by 10 orders of magnitude by treating oleic acid-coated CQDs with much shorter hydrazine. Investigating the inter-particle separation for a variety of different ligands, Weidmann et al. found that monothiol- and dithiol-based ligands result in spacings approximately equal to the length of a single ligand. Crucially, those ligands, which lead to shortest distances, are not the ones commonly employed in efficient opto-electronic devices. This underlines that further aspects of the ligand-CQD interaction, such as doping, energy level positions and -alignment (consider section 2.4.4), as well as trap distributions, are relevant for the device performance. Different ligands will furthermore also give rise to different heights of the tunnelling barrier $\Delta E$ between the CQDs, which will also impact the inter-particle coupling even if their spacing remains unchanged.

Additional to the separation and barrier height, the CQD size also affects the coupling of CQDs. A monotonic increase in hole mobility was reported upon increasing the CQD size, whilst the electron mobility exhibited a peak at a particle diameter of 6 nm. The latter was attributed to a trade-off between the reduced activation energy (lower hopping barrier $\Delta E$) and weakened inter-dot coupling strength amongst larger CQDs.

Since the energy levels in CQDs are linked to the size of the particle ($\propto r^{-2}$; equation 2.14), a finite size-distribution also leads to a distribution of energy levels, i.e. above mentioned (diagonal) disorder, within the CQD solid. Disorder can furthermore arise due to differences of the
CQD separation $\Delta x$ (site- or off-diagonal disorder), which affects the wavefunction coupling. Charge transfer between two CQDs is most efficient for equal energies (resonant tunnelling), else phonons are needed to assist the transfer and the transition rate drops strongly for increasing disorder.\textsuperscript{[201]}

For highly regular assemblies of strongly coupled CQDs, the discrete states are expected to split and form electronic (mini-)bands, which were proposed to exhibit a width of up to several hundreds of meV.\textsuperscript{[214-215]} The high mobilities (10-30 cm$^2$/Vs) observed for some inorganic ligands\textsuperscript{[216-217]} or ammonium thiocyanate ligands\textsuperscript{[218]} were considered suggestive of band formation.\textsuperscript{[219]} Indeed, a delocalisation of electrons was observed for epitaxially fused CQD solids,\textsuperscript{[220]} noting that an even higher degree of order would lead to band-like transport.\textsuperscript{[220]} Moreover, a sometimes observed increasing mobility at low temperatures was assumed to point to band rather than hopping transport. But it was also argued that such a behaviour could be readily explained by hopping transport.\textsuperscript{[205]}

The self-assembly of CQDs depends on many factors, including solvent evaporation rate,\textsuperscript{[221]} CQD size and size-distribution (supperlattices can only form for a polydispersity $\leq$5%), the interactions between the CQDs themselves or the substrate,\textsuperscript{[222]} and the number and type of surface ligands. This plethora of impacts offers the opportunity to deliberately engineer the CQD assembly. Spin- or drop-casting films typically leads to a short-range order, i.e. each CQD is surrounded by the same number of nearest neighbours.\textsuperscript{[172]} As-synthesised oleic acid-passivated PbS CQDs, for example, were reported to be able to form a two- to three-dimensional cubic superlattice arrangement.\textsuperscript{[223-224]} Subsequent treatment with different ligands can change this order and form a tetragonal lattice or a disordered isotropic phase depending on the ligand concentration.\textsuperscript{[223]} An epitaxial merging of nearest neighbours leading to a strong interaction was furthermore observed for different ligands (iodide-based, sodium sulphide, amines),\textsuperscript{[224-225]} noting that not only the ligands themselves, but also the counterions and the acidity of the environment affect the superlattice formation. Based on these achievements, the actual growth mechanism of superlattices has recently been moved into the focus of attention.\textsuperscript{[226]} Despite such success, it has to be noted, though, that strong necking of CQDs and their close proximity can also lead to a vanishing of the quantum confinement, which is rarely desired.

\subsection*{2.4.4 Surface Chemistry}

As-synthesised CQDs are capped with long aliphatic chains, such as oleic acid (OA) or oleylamine (OAm)s. The exchange towards shorter ligands, as discussed above, is commonly driven by several forces, of which the stronger coordination of the anchoring group is the most obvious. Given their strong coordination, short thiol-containing molecules have for a long time been the most commonly used materials for this purpose. Most importantly for this thesis, these include variants of benzenedithiol (BDT) (consider Figure\textsuperscript{[2.23]} (a)), of which 1,4-BDT sho-
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wed the best performance in Shottky-type solar cells. Similarly, 1,2-ethanedithiol (EDT) or 1,3-mercaptopropionic (MPA) are frequently applied ligands. These molecules share that they exhibit anchoring groups on two opposite sides and can thus couple two CQDs together. More recently, halide ions from organo-halide salts, such as tetrabutylammonium iodide or -chloride have been employed, which allow for even shorter inter-particle distances and the manufacturing of air-stable CQD films.

So far, as-synthesised PbS CQDs were discussed as being covered uniformly by oleic acid molecules. This is a simplification, since the different facets of the PbS crystals also behave differently. Oleic acid only covers the "chequerboard"-presenting (001) facet, which is terminated by alternating lead and sulphur atoms. The polar (111) facet, in contrast, terminated only by Pb atoms, is covered by oleate and hydroxyl groups. The Pb-termination of the (111) facet suggests a lead-rich surface of CQDs and as-synthesised CQDs were indeed reported to be non-stochiometric with an excess of Pb. A deviation from a balanced stochiometry in CQDs, however, is expected to lead to doping. For PbS, in which Pb is in its +2 and S in its -2 oxidation state, this leads to n-doping for excess lead and p-doping for excess sulphur (consider Figure 2.23 (b)). Also, unlike to bulk materials, surface modification of CQDs can have a profound effect on the CB and VB density of states and thereby shift the Fermi energy within the band gap.

While as-synthesised CQDs without surface ligands would thus be of strong n-type with many surface traps, the presence of binding surface ligands, typically with negative charge, also changes the partial charges (oxidation states) of surface atoms and can passivate possible trap states. Careful choosing of the surface anchoring group thus allows to significantly change the electronic properties of CQDs. Most prominently, this technique was employed to create a p-n-homojunction in PbS CQDs solar cells by employing a layer of EDT terminated PbS on top of a layer of tetrabutylammonium iodide (TBAI) capped PbS. Proving this effect, direct tuning of the CQD stoichiometry to move the doping level has furthermore been achieved via deposition of excess metal atoms onto the surface of CQDs. Besides affecting the doping level and density of electronic states, surface ligands may also introduce significant shifts of energy levels due to surface dipoles (Figure 2.23). Changing the position of the valence and conduction levels of CQDs with respect to vacuum has been reported in several investigations, and can play a crucial role for proper energy level alignment in devices.

Additional to these deliberate changes in CQD surface chemistry, exposure of the materials to the environment can also affect the surface coverage and electronic properties. Long air exposure, for example, was reported to lead to the formation of PbSO_{3} and PbSO_{4}, and reversible O_{2} adsorption was reported to create states within the band gap of PbS CQDs. Trap states in CQDs are detrimental for electronic applications. Their formation and origin was addressed in a wide range of different experimental and theoretical works. Besides co-
Figure 2.23: Different ligands can be used to cover the surface of PbS CQDs (a). The position of the Fermi level in CQDs can be shifted by surface treatments (b). Dipoles introduced by ligands can also shift the absolute position of CQD energy levels with respect to vacuum. Adapted from Ref. [236].

vering PbS CQDs with a shell of inorganic wide-bandgap material to suppress the trap formation, [247,248] intricate multi-ligand strategies were employed to passivate as many traps as possible. [249–251]
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