

obtained by GE Global Research in 2013. The open circuit voltage of this cell is 857.3 mV, the short circuit current density is 28.59 mA/cm<sup>2</sup>, and the FF is 80.0%. The current record module based on CdTe technology has a conversion efficiency of 16.1% at an area of 7200 cm<sup>2</sup>.

The current cost of modules from First Solar product is in the order of 0.68 to 0.70 USD/W<sub>p</sub> and is expected to drop to 0.40 USD/W<sub>p</sub>, hence keeping the cost per W<sub>p</sub> lower than that of modules based on crystalline silicon wafers.

An important aspect that needs to be addressed is the toxicity of cadmium. However, insoluble Cd compounds like CdTe and CdS are much less toxic than the elementary Cd. Nonetheless, it is very important to prevent cadmium entering into the ecosystem. It is an important question whether, CdTe modules could become a major source of Cd pollution. As of 2014, First Solar has an installed *nameplate capacity* of 1.8 GW<sub>p</sub>/year.[85] With this capacity, about 2% of the total industrial Cd consumption would be taken by First Solar. Nevertheless, recycling schemes have been set up for installed CdTe solar modules. For example, First Solar has a recycling scheme in which a deposit of 5 dollar cents per W<sub>p</sub> is included to cover the cost for the recycling at the end of the module lifetime.

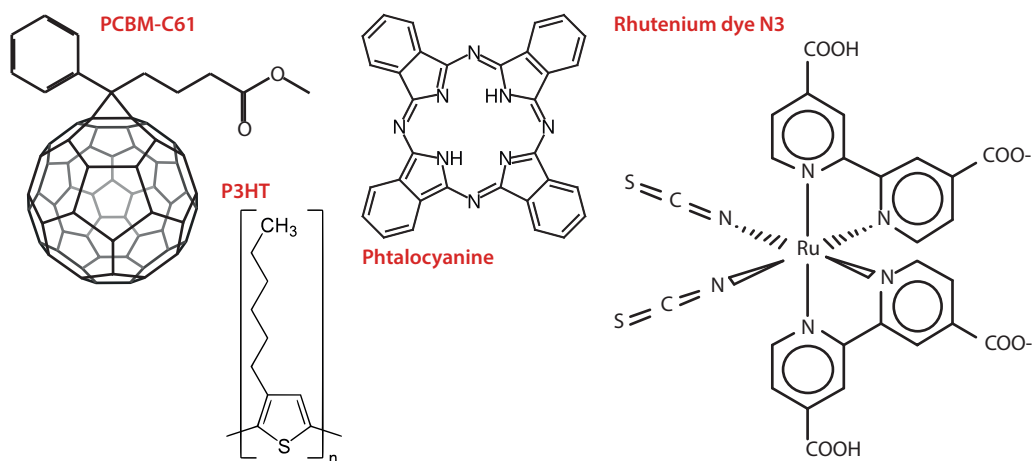
Maybe an even bigger challenge for the CdTe technology is the supply with tellurium. Let us take another look at Fig. 13.1 that shows the abundance of the various elements in the Earth's crust. Tellurium is one of the rarest stable solid elements in the Earth's crust with an abundance of about 1 µg/kg, which is comparable to that of platinum [86]. Because of its scarcity, the supply with Te might be the limiting step to upscale the CdTe PV technology to future terawatt scales. On the other hand, Tellurium as source material has only had a few users so far. Thus, for Te no dedicated mining has been explored so far. In addition, new supplies of tellurium-rich ores were found in Xinju, China. In conclusion, at this moment it remains unclear to which extent the CdTe PV technology might be limited by the supply with tellurium.

## 13.5 Organic photovoltaics

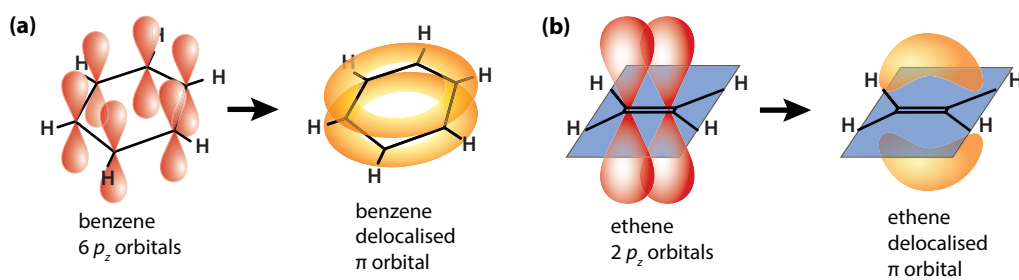
So far we discussed inorganic thin-film semiconductor materials such as III-V semiconductors, amorphous and nanocrystalline silicon, CIGS and CdTe solar cells. In this section we will take a look at *organic photovoltaics*. The used absorber materials are either *conductive organic polymers* or *organic molecules* that are based on carbon, which may form a cyclic, a-cyclic, linear or mixed compound structure.

Figure 13.23 shows some example of organic materials that can be used for PV applications: P3HT, Phtalocyanine, PCBM and Ruthenium Dye N3. All these materials can be considered as large conjugated systems, which means that carbon atoms in the chain have an alternating single or a double bond and every atom in the chain has a p-orbital available. In such conjugated compounds, the p-orbitals are delocalised, which means that they can form one big mixed orbital. Hence, the valence electron of the original p-orbital is shared over all the orbitals. A classical example would be the benzene molecule, which is a cyclic conjugated compound. As we can see in Fig. 13.24 (a), This molecule has 6 carbon atoms and six p-orbitals, which mix and form two circular orbitals that contain three electrons each. These electrons do not belong to one single atom but to a group of atoms.

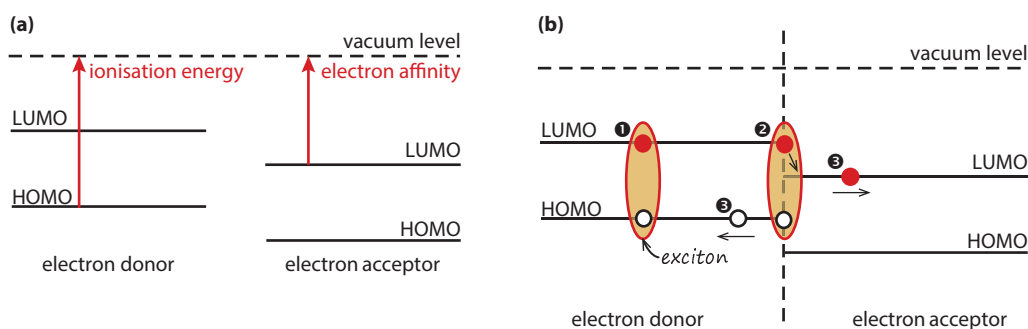
In contrast, a methane molecule (CH<sub>4</sub>) is tetrahedrally coordinated, which means that it



**Figure 13.23:** Some examples of organic molecules used for organic photovoltaics.



**Figure 13.24:** The chemical structure and  $\pi$  orbitals of (a) benzene and (b) ethene.



**Figure 13.25:** Illustrating (a) the energy levels in organic PV materials and (b) the separation of electrons and holes in an exciton at the acceptor-donor interface..

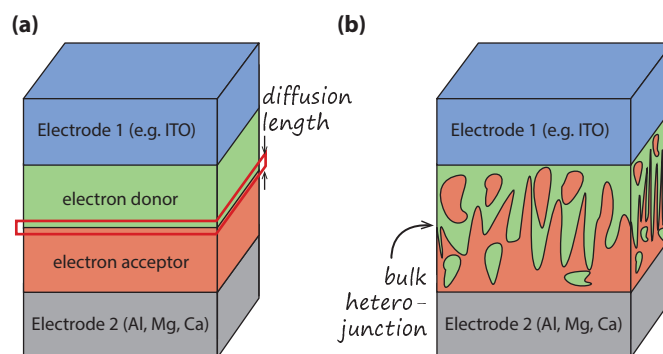
has 4 equivalent  $sp^3$  hybrid bonds with a bond angle of  $109.5^\circ$ . An ethene ( $C_2H_4$ ) molecule has three equivalent  $sp^2$  hybrid bonds with a bond angle of  $120^\circ$  plus an electron in a  $p^z$  orbital. Two neighbouring  $p^z$  orbitals form a so-called  $\pi$  orbital, as illustrated in 13.24 (b).

In Chapter 6 we have discussed that two individual  $sp^3$  hybrid orbitals can make an anti-bonding and a bonding state. The same is valid for the two  $p^z$  orbitals forming a molecular  $\pi$  orbital. They can make bonding and anti-bonding  $\pi$  states. Therefore, conjugated molecules can have similar properties as semiconductor materials.

At room temperature, most electrons are in the bonding state, which is also called the *highest occupied molecular orbital* (HOMO). The anti-bonding state can be considered as the *lowest unoccupied molecular orbital* (LUMO). As the conjugated molecules are getting longer, the HOMO and LUMO will broaden and act similar to valence and conduction band in conventional semiconductors. The energy difference between the HOMO and LUMO levels can be considered as the bandgap of the polymer material.

To discuss whether an organic material is *p*-type or *n*-type, we first have to introduce the concept of the *vacuum level*, shown in Fig. 13.25 (a). The vacuum level is defined as the energy of a free stationary electron that is outside of any material, or in other words, *in vacuo*. This level often is used as the level of alignment for the energy levels of two different materials. The *ionisation energy* is the energy required to excite an electron from the valence band or HOMO to the vacuum state. The *electron affinity* is the energy obtained by moving an electron from the vacuum just outside the semiconductor or conjugated polymer to the bottom of the conduction band or LUMO. When a material has a low ionisation potential, it can release an electron out of the material relatively easy, *i.e.* it can act as an *electron donor*. On the other hand, when a material has a high electron affinity, it can easily accept an additional electron in the LUMO or conduction band, it thus acts as an *electron acceptor*.

As we have discussed earlier, in inorganic semiconductors an electron can be excited from the valence band to the conduction band leaving a hole in the valence band. Such an electron-hole pair is only weakly bound and both entities are easily separated and can diffuse away from each other. In organic materials this is not the case. Absorption of a photon with sufficient energy results in the creation of an *exciton*, illustrated in Fig. 13.25 (b) ①. An exciton is an excited electron-hole pair that is still in bound state because of the mutual Coulomb forces between the particles. Such excitons can diffuse through the



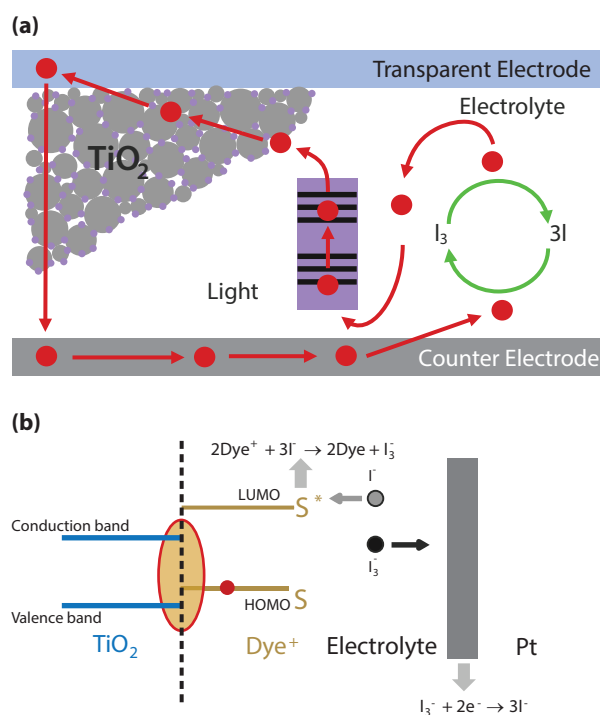
**Figure 13.26:** Illustrating (a) the layer structure of organic solar cells and (b) an organic solar cell with a *bulk heterojunction*.

material, but they have a low life time in organic materials, recombining back to the ground state within a few nanoseconds. Hence, the diffusion length of such excitons is in the order of only 10 nm.

If an electron donor and an electron acceptor material are brought together, an interface is formed between those two. The HOMO and LUMO of both polymers can be aligned considering their energy levels with reference to the vacuum level, as illustrated in Fig. 13.25 (b). At the interface we see a difference in the HOMO and LUMO levels. Because of this difference, an electrostatic force exists between the two materials. If the materials are chosen such that the difference is large enough, these local electric fields can break up the exciton  $\ominus$ . The electron then can be injected into the electron acceptor and a hole remains in the electron donor material  $\oplus$ .

Figure 13.26 (a) shows the structure of a typical organic solar cell. Here, we consider a solar cell consisting of both organic acceptor-type and donor-type materials. Similar as for semiconductor materials, a heterojunction based on two different materials or conjugated compounds can be constructed. As mentioned before, the typical diffusion length in the organic materials is only about 10 nm. Hence, the thickness of the solar cell in principle is strongly limited by the diffusion length, while it has to be at least 100 nm to absorb a sufficient fraction of the light. Therefore, organic solar cells are based on *bulk heterojunction* photovoltaic devices that is illustrated in Fig. 13.26 (b), where the electron-donor and the electron-acceptor materials are mixed together and form a *blend*. In this way, typical length scales in the order of the exciton diffusion lengths can be achieved. Hence, a large fraction of the excitons can reach an interface, where they are separated into an electron and a hole. The electrons move through the acceptor material to the electrode and the holes move through the donor material to be collected at the other electrode. Usually, the holes are usually collected at a TCO electrode, for example *indium tin oxide* (ITO). The electrons are collected at a metal back electrode.

Chemical engineering allows to tune the bandgap. Advantages of organic solar cells are that they have low production costs and that they can be integrated into flexible substrates. Important disadvantages are a low efficiency, low stability and low performance compared to inorganic PV cells.



**Figure 13.27:** (a) A sketch of a dye sensitised solar cell and (b) the relevant energy levels in its operation.

Although organic solar cells themselves can be cheap, they require expensive encapsulation materials to protect the organic materials from humidity, moisture and air, which limits the industrial application. To the authors' knowledge, no company is currently producing organic PV modules. In the past, the U.S. based company Konarka Technologies produced small PV modules with efficiencies in the range of 3 up to 5%, which worked for a couple of years only.

The reported record organic solar cells is 11.1% and was achieved by Mitsubishi chemicals [77].

## 13.6 Hybrid organic-inorganic solar cells

In this section we discuss two hybrid concepts, where the junction consists of both inorganic and organic compounds. These concepts are *dye-sensitised solar cells* and *perovskite solar cells*.

### 13.6.1 Dye-sensitised solar cells

An alternative solar cell concept based on organic materials is the dye-sensitised solar cell (DSSC), which is a photoelectrochemical system. It contains *titanium dioxide* ( $\text{TiO}_2$ ) nanoparticles, organic *dye* particles, an electrolyte and platinum contact. Figure 13.27 (a) shows an illustration of a DSSC. The dye sensitiser, which acts like an electron donor, is the photoactive component of the solar cell. The second major component are the  $\text{TiO}_2$  nanoparticles that act as the electron-acceptor. Similar to organic bulk heterojunction cells, the dye is mixed with  $\text{TiO}_2$ .

As a photoactive dye sensitiser, *ruthenium polypyridine* is used. The operation is illustrated in 13.27 (b). If a photon is absorbed by the ruthenium polypyridine, it can excite an electron from its ground state, the  $S$  state, to an excited state, referred to as  $S^*$ . In this case the  $S$  can be considered as a HOMO and the  $S^*$  state can be considered as LUMO. The  $S^*$  energy level is above the energy level of the conduction band of the  $\text{TiO}_2$ . As a result, the light excited electrons are injected into the  $\text{TiO}_2$  nanoparticles, while the dye-sensitiser molecule remains positively charged. The electrons move through the  $\text{TiO}_2$  to the TCO based back contact in a diffusion based transport mechanism. Via the electric circuit, the electrons move to the front contact. The front contact is electrically connected to the dye via an *electrolyte*. Electrolytes are solutions or compounds that contain ionised entities that can conduct electricity. The typical electrolyte used for DSSC contains *iodine*. The positively charged oxidised dye molecule is neutralised by a negatively charged iodide. Three negatively charged iodides, neutralise two dye molecules and create one negatively charged tri-iodide. This negatively charged tri-iodide moves to the counter electrode where it is reduced using two electrons into three negatively charged iodide. To facilitate the chemical reactions, these *photoelectrochemical* cells require a *platinum* back contact.

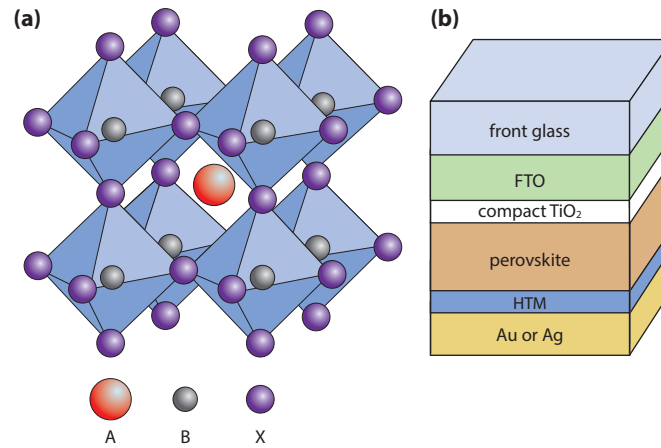
The performance of a DSSC depends on the HOMO and LUMO level of the dye material, the Fermi level of  $\text{TiO}_2$  nanoparticles and the *redox potential* of the iodide and triiodide reactions. The current record efficiency of dye-sensitised PV devices on lab-scale is 11.9% and was achieved by Sharp [77].

The major advantage of DSSC are the low production costs. A disadvantage is the stability of the electrolyte under various weather conditions: At low temperatures the electrolyte can freeze, which stops the device from generating power and might even result in physical damage. High temperatures result in thermal expansion of the electrolyte, which make encapsulating modules more complicated. Another challenge is the high cost of the platinum electrodes, hence replacing the platinum with cheaper materials is a topic of ongoing research. Secondly, more stable and resistive electrolyte materials must be developed. Thirdly, research is done on improved dyes that enhance the spectral and bandgap utilisation of the solar cells.

Yet, no dye-sensitised PV products are available commercially.

### 13.6.2 Perovskite solar cells

A rapidly emerging PV technology is that of *perovskite solar cells* that has seen a tremendous increase in initial efficiency in recent years. In 2006, perovskite cells with 2.2% were reported in 2006. Cells with 6.5% were reported in 2011 and since then the reported efficiencies rapidly increases with an actual (October 2014) certified record efficiency of 17.9% [77, 87].



**Figure 13.28:** (a) A sketch of the perovskite crystal structure with the anion X and the cations A and B indicated (adapted by permission from Macmillan Publishers Ltd: M. A. Green, A. Ho-Baillie, and H. J. Snaith, *Nature Photonics*, vol. 8, pp. 506-514, copyright (2008)) [87]. (b) The layer structure of a thin-film based perovskite solar cell.

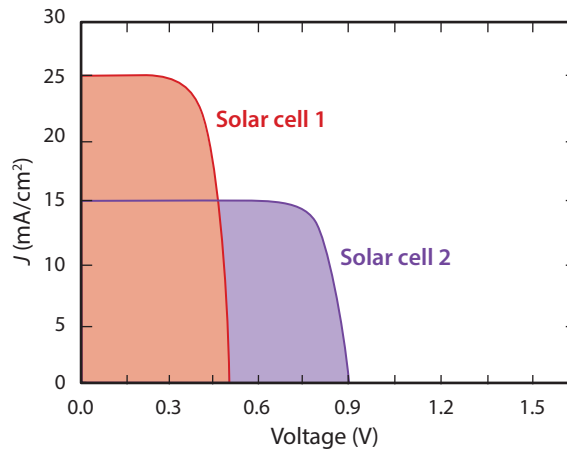
The mineral perovskite is named after the Russian mineralogist Lev A. Perovski (1792-1856) and has the chemical formula  $\text{CaTiO}_3$ . For solar cells, not this mineral is used, but minerals with the general formula  $\text{ABX}_3$ , where X is an anion, and both A and B are cations. A is larger than B [87]. Minerals with this structure are called *perovskites*. Figure 13.28 (a) shows the general cubic crystal structure of perovskites.

For photovoltaics, organic-inorganic perovskites are used, where the large cation A is organic; often methylammonium ( $\text{CH}_3\text{NH}_3^+$ ) is used. X is a halogen, such as iodine, chlorine, or bromine, often in a mixed halide material. The cation B usually contains lead (Pb). While also tin (Sn) can be used, which theoretically gives even more ideal bandgaps, the stability usually is lower. When using these compounds (A:  $\text{CH}_3\text{NH}_3^+$ , B: Pb, X: I), the total compound is called *methylammonium lead triiodide* and has the chemical formula ( $\text{CH}_3\text{NH}_3\text{PbI}_3$ ).

Figure 13.28 (b) shows the structure of a typical thin-film perovskite-based solar cell [87]. On fluorine-doped tin oxide (FTO) a compact titanium dioxide ( $\text{TiO}_2$ ) is deposited, via this electrons are transported to the FTO layer. The perovskite layer is then deposited onto this  $\text{TiO}_2$  layer and covered by a hole-transporting material (HTM). On top of the HTM, silver or gold is placed as a back metal. Besides thin-film architectures, also mesoporous architectures are used, where the perovskite is present in a porous  $\text{TiO}_2$  layer.

Perovskite materials used for solar cells have several properties that enable the high efficiencies: they have a very strong absorption of the incident light combined with low non-radiative carrier recombination. Further, their development can build on more than 20 years of experience from the development of organic and dye-sensitised solar cells [87].

All current high-efficiency perovskite devices contain lead. This might be a problem because Pb is toxic. However, as we have seen above, CdTe technology is currently very successful, despite the toxic cadmium that is required to make these PV devices. Another



**Figure 13.29**

issue is degradation of the cells due to ultraviolet radiation and/or moisture. This degradation can be quite fast [87] and is an issue that clearly must be solved if this technology should be applied industrially.

Measuring the  $J$ - $V$  characteristics of perovskite cells needs to be done carefully, because of *hysteresis*: depending on the voltage scan direction (from high to low or from low to high voltages) and the scan speed, the shape of the measured  $J$ - $V$  curve can change significantly. This can lead to an overestimation or an underestimation of the device performance [88].

## 13.7 Exercises

- 13.1 Figure 13.29 shows the  $I$ - $V$  curves of two single junction solar cells. If you were to make a multi-junction solar cell with these two cells, which one would you put as a top cell?
- 13.2 In Fig. 13.10 we have the bandgap versus the lattice constant of various III-V materials. Which of the following statements is true?
- The junctions of a lattice-matched triple junction solar cell can be based on the semiconductor materials GaInP, GaAs and Si.
  - If the bottom cell of a 4-junction cell is based on Ge, the first junction above the bottom cell is based on GaInAs.
  - A combination of three junctions based on the semiconductor materials GaInP, GaAs and Ge can only result in a metamorphic triple junction solar cell.
  - The semiconductor material InAs is a logic choice to be used as a top cell in a triple junction.
- 13.3 Why an a-Si:H solar cell cannot rely on diffusion to separate the photo-generated carriers as much as a c-Si solar cell does?
- The higher bandgap (around 1.7 eV) prevents the photo-generated carriers from diffusing through the intrinsic layer of the a-Si:H cell.