



Review

Organic photovoltaics: Potential fate and effects in the environment

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ABSTRACT

In times of dwindling fossil fuels it is particularly crucial to develop novel “green” technologies in order to cover the increasing worldwide demand for energy. Organic photovoltaic solar cells (OPVs) are promising as a renewable energy source due to low energy requirement for production, low resource extraction, and no emission of greenhouse gases during use. In contrast to silicon-based solar cells, OPVs offer the advantages of light-weight, semi-transparency and mechanical flexibility. As to a possible forthcoming large-scale production, the environmental impact of such OPVs should be assessed and compared to currently best available technologies. For the first time, this review compiles the existing knowledge and identifies gaps regarding the environmental impact of such OPVs in a systematic manner. In this regard, we discuss the components of a typical OPV layer by layer. We discuss the probability of enhanced release of OPV-borne components into the environment during use-phase (e.g. UV- and biodegradation) and end-of-life phase (e.g. incineration and waste disposal). For this purpose, we compiled available data on bioavailability, bioaccumulation, biodegradation, and ecotoxicity. Whereas considerable research has already been carried out concerning the ecotoxicity of certain OPV components (e.g. nanoparticles and fullerenes), others have not been investigated at all so far. In conclusion, there is a general lack of information about fate, behavior as well as potential ecotoxicity of most of the main OPV components and their degradation/transformation products. So far, there is no evidence for a worrying threat coming from OPVs, but since at present, no policy and procedures regarding recycling of OPVs are in action, in particular improper disposal upon end-of-life might result in an adverse effect of OPVs in the environment when applied in large-scale.

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1. Introduction

Due to the future prospects that mankind will be running short of energy resources derived from fossil fuels within this century, the conversion of solar energy by means of a wide variety of different photovoltaic solar cells has become of increasing interest in society, politics, economy and scientific research during the last decade (Roncali, 2009). Whereas the world's annual energy consumption has approximately doubled from 1971 to 2009 – from about 4.000 to 8.000 million tons of oil equivalent (Mtoe) per year –, in the same timespan the electricity consumption even more than tripled (from about 400 to 1.400 Mtoe) (International Energy Agency, IEA, 2011). In consideration of a continuative increase in energy demand, there is an urgent need for new energy-delivering technologies with low impacts on the environment. First generation photovoltaic solar cells based on crystalline silicon are already a well-established alternative for fossil fuels and especially advantageous concerning emission of greenhouse gasses (García-Valverde et al., 2010). Even though power conversion efficiencies of up to 14% and lifetimes of more than 20 years are reached (García-Valverde et al., 2010), such solar modules have their shortcomings: high energy consumption during production procedures is resulting in energy payback times of about one to two years and high production costs. Additionally, typical characteristics such as

heavy weight, mechanical inflexibility and the lack of transparency are constraining their applications (Zhou et al., 2010). As a consequence of this, organic photovoltaic solar cells (OPVs) based on organic polymers – therefore also called “plastic solar cells” – are seen as promising alternative overcoming most of the shortcomings of established silicon solar cells. Advantages include little consumption of scarce materials such as indium (European Commission, 2010) and low energy consumption during deposition processes (Miles et al., 2005). Furthermore, due to OPV's thin layer constitution, semi-transparency, mechanical flexibility and low weight (about 0.5 kg m⁻²), their applicability is almost unlimited; for instance, integration in clothing or large-area coating of even nonplanar glass fronts (Roes et al., 2009). Although being a product not even 20 years old (Yu et al., 1995), OPVs with lifetimes of a few years and energy payback times of about two to four years (García-Valverde et al., 2010), as well as maximal power conversion efficiencies of up to 10% (National Renewable Energy Laboratory, NREL, 2012) have been developed, underlining the promising trend towards market competitiveness. To date, thin film technology solar cells, showing the same beneficial characteristics (e.g. mechanical flexibility), do not require more energy during production, have shorter energy payback times (about 0.75 to 2 years) (García-Valverde et al., 2010), and reach very high power conversion efficiencies of up to 20.3% (National Renewable Energy Laboratory, NREL, 2012). However, their drawback in contrast to OPVs is the consumption of scarce and potentially harmful elements such as cadmium, tellurium, indium, and gallium. In conclusion, OPVs seem to be a very promising technology replacing conventional energy producing systems.

In order to optimize the lifetimes, power conversion efficiencies, and ultimately the levelized costs of electricity to competitive levels, a variety of different OPVs has been developed so far, such as bulk-heterojunction solar cells (Deibel et al., 2010; Sariciftci et al., 1992), tandem polymer solar cells (Ameri et al., 2009; Hadipour et al., 2008; Kim et al., 2007; Siddiki et al., 2010; Sista et al., 2011), and dye-sensitized solar cells (Grätzel, 2009; Nazeeruddin et al., 2011; O'Regan and Grätzel, 1991). Here, we focus on established bulk-heterojunction solar cells since efforts have recently been done to place them on the market and they can be reasonably expected to be environmentally relevant now and in the near future. Since a variety of different types of bulk-heterojunction OPVs has been developed until now, a multitude of different materials has been used (Coakley and McGehee, 2004; Scharber et al., 2006). However, a detailed discussion of all materials used during development would exceed the dimension of a review, hence, it is necessary to focus on materials commonly used in practice (Deibel et al., 2010). In Fig. 1 the structure of such a typical OPV can be seen: typically, on the sun-facing side, a transparent substrate such as glass (inflexible) or plastic (flexible) is protecting the cell against UV-light, moisture and oxygen (Section 2.1). This substrate is coated with a conductive material working as the anode (Section 2.2). This structure is followed by a layer of a polymer acting as electron-hole transporting layer (Section 2.3). The light-absorbing active layer is composed of a blend of an organic polymer acting as the electron-donor (Section 2.4) and an electron-acceptor (Section 2.5). The structure is finished by an electron transporting layer

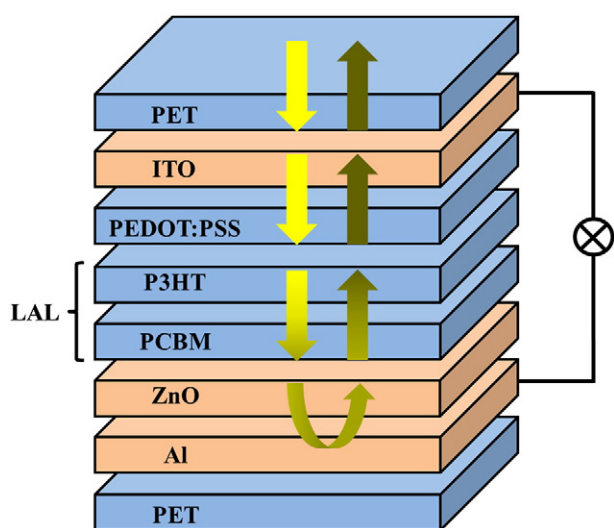


Fig. 1. Structure of a typical bulk-heterojunction solar cell, adapted from materials commonly in use (Deibel et al., 2010). Organic layers are colored in gray, inorganic layers in white. The sunlight is absorbed in the light-absorbing layer (LAL) before and after being reflected at the aluminum (Al) cathode. PET – substrate/package; ITO – anode; PEDOT:PSS – electron-hole transporting layer; P3HT – electron-donor; PCBM – electron-acceptor; and ZnO – electron transporting layer. For abbreviations: see corresponding chapters.

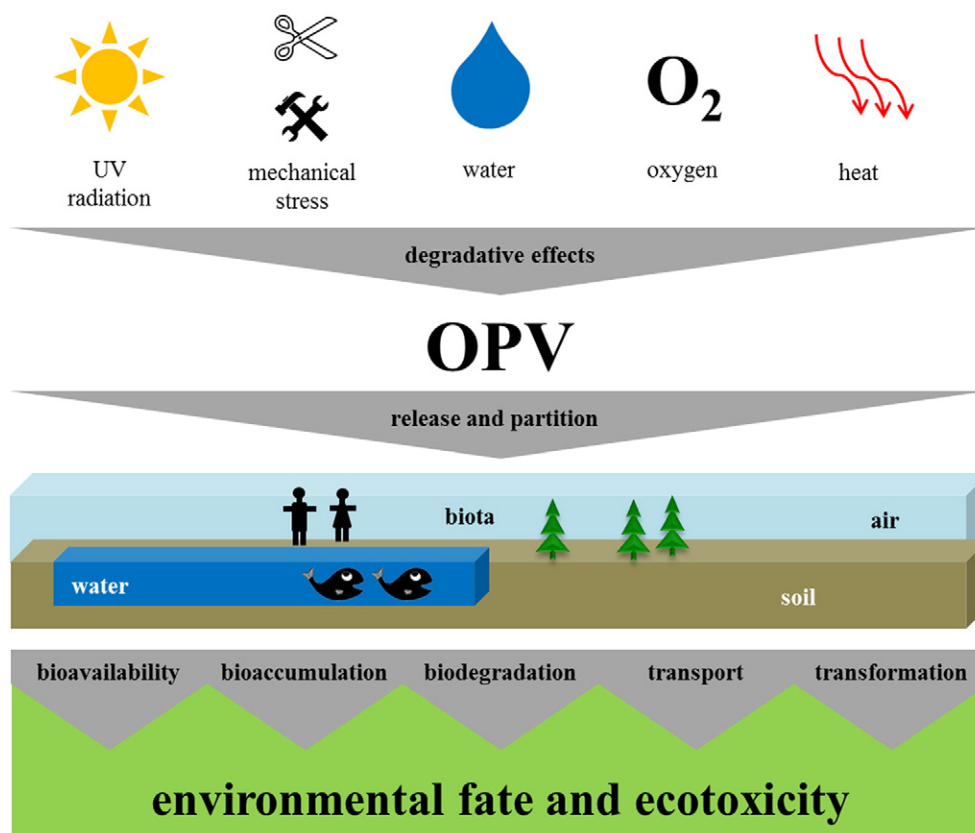


Fig. 2. Different factors can have a degradative effect on OPVs leading to aging of the material and possibly cause the release of potentially hazardous compounds into the environment. After partition of those compounds into air, water, soil, and biota, processes such as bioaccumulation or biodegradation determine their fate and ecotoxicological impacts.

(Section 2.6) (Gilot et al., 2007) and a metallic cathode (Section 2.7). Optionally, an optical spacer can be inserted (Section 2.6) leading to increased power conversion efficiencies (Kim et al., 2006).

In addition to this restriction of possible OPV materials, it is not the aim of this overview to carry out a whole life cycle assessment “from cradle to grave” since such assessments been published recently (Azzopardi et al., 2011; Espinosa et al., 2011a,b, 2012a,b). Hence, this study is limited to processes occurring to the finished OPV product during use and end-of-life phase scenarios. As a consequence of this, aspects present during production of raw materials, production of the OPV, transport, or consumption of energy and chemicals for disposal and recycling processes are not considered within this literature review. In Fig. 2, a scheme of the environmental impact of OPVs is drawn, beginning with destructive factors on OPVs, possible leaching and partitioning of OPV components and assumed processes happening when reaching the environment. Until now, the fate of OPVs and their single components in the environment has not been systematically investigated. Therefore, it is necessary to carry out more research and to assess the environmental and health impacts of such a promising future energy-supplier. In this review, we discuss one typical bulk-heterojunction OPV layer after another and we raise issues such as:

- What degradation processes do OPV components undergo?
- What are the maximal environmental concentrations which can be expected to be released from OPVs?
- Which fate do they meet in the environment and what are the possible ecotoxic effects? Which end-of-life scenario enhances the release of which component?
- Finally, we identify gaps in knowledge necessary to fully assess the potential impact of such OPVs.

2. OPV composition

2.1. Substrate: PET

2.1.1. Degradation/liberation processes and environmental fate

Since the functional layers converting sunlight into electrical power are sensitive against oxygen, moisture, and temperature, they are often embedded in poly(ethylene-terephthalate) (PET) maintaining the mechanical flexibility of the OPVs. PET as the packaging material as well as flexible substrate for large throughput production is the major component in OPVs (cf. Table 3). This organic polymer is classified as a semi-crystalline polymer from the polyester family with a glass temperature of about 72 °C and is manufactured from terephthalic acid and ethylene glycol ($n = 130\text{--}150$) (Sinha et al., 2010). Due to its supreme characteristics regarding light weight, transparency, gas-impermeability, mechanical stability, persistence, and cheap production costs, PET is accounting for more than 50% of the world's synthetic fiber manufacture and its consumption for packaging purposes (e.g. PET bottles for beverages) was an estimated 17 billion dollars in 2010 (Sinha et al., 2010). Worldwide, an estimated 15 million tons of PET are produced every year, 3.5 million tons of which are used for packaging purposes, among which are mainly bottles (Reis and Carneiro, 2012). Since PET possesses a high durability and long persistence against environmental stress, the immense production volumes and large amounts of PET dumped or incinerated in an uncontrolled manner represent a major environmental problem (Moore, 2008).

If not recycled or incinerated under controlled conditions, PET is usually burned in uncontrolled open fires, littered in landfills or just thrown away into the terrestrial environment from where it can reach aquatic systems such as the oceans. Recent reports show, that remarkable

29.1% of all PET bottles and cans were collected and recycled in the U.S. (National Association for PET Container Resources, NAPCOR, 2011), whereas 55.6% of all consumed PET is recycled in Brazil (Reis and Carneiro, 2012). Apart from fragmentation of the PET waste into smaller pieces, this polymer is considered to be non-biodegradable under environmental conditions (Kint and Muñoz-Guerra, 1999). Until today only modified polyethylene structures are partially biodegradable and only under a simultaneous partial loss of their advantages such as dynamical stiffness (Luckachan and Pillai, 2011). Polymer biodegradation includes on the one hand its depolymerization associated with microorganisms and their secretion products and on the other hand the degradation through environmental processes such as oxidation, hydrolysis, thermal degradation, and photo-degradation (Wang et al., 2003). In order to make non-biodegradable polymers such as PET biodegradable, different methods were developed, e.g. synthetic polyester blends, aromatic-aliphatic copolyesters or starch-based blends (Müller et al., 2001; Okada, 2002; Wang et al., 2003; Zheng et al., 2005). Additionally, natural photo-degradation was studied. As a consequence of long-term sunlight exposure, PET-monomers, PET-monomer fragments as well as PET-dimer fragments were found on the sunlight-facing side of PET pieces in not investigated quantities (Wegelin et al., 2001). As a conclusion, there is a trade-off, since from an environmentally point of view biodegradable PET is preferable, but the most important characteristic of PET for OPV applications is persistence in order to make OPVs as durable as possible.

2.1.2. Ecotoxicity

PET is disposed as macroscopic structures into the environment and remains there very persistently over a long time. This polymer is not considered to be directly toxic. However, when PET is disintegrating into small parts, these pieces can reach the same size range as the natural food of larger organisms. Consequently, organisms feed on plastic leading to adverse effects or starvation. Microplastics accumulate in organisms like mussels (Browne et al., 2008), fishes (Boerger et al., 2010), fur seals (Eriksson and Burton, 2003) and birds (Van Franeker et al., 2011). Furthermore, such mobile plastic particles can sorb other persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT), polycyclic aromatic hydrocarbons (PAHs), and aliphatic hydrocarbons, which makes these POPs more bioavailable for organisms upon ingestion (Andrady, 2011; Rios et al., 2007, 2010).

During PET production procedures, metallic catalysts are used for polymerization. Antimony as well as titanium, cobalt, germanium, manganese, magnesium and zinc are employed. It has been shown in different studies that antimony may leach from PET drinking bottles (Cheng et al., 2010; Welle and Franz, 2011), e.g. into commercially available juices in concentrations even above the EU limitations for drinking water (Hansen et al., 2010). A clear relationship between increased temperature and augmented antimony leaching was shown in PET bottles (Westerhoff et al., 2008), which indicates that OPVs, which are exposed to high temperatures when facing direct sunlight, could potentially release antimony as well as other heavy metals at ppb levels.

Besides heavy metals, phthalates used as plasticizers may leach from PET bottles, even though detected $3.52 \mu\text{g L}^{-1}$ phthalates did not reach prescriptive limits (Montuori et al., 2008). Considerable research was carried out about phthalates and other endocrine-disrupting chemicals potentially leaching from PET bottles (Diana and Dimitra, 2011; Guart et al., 2011; Schmid et al., 2008; Wagner and Oehlmann, 2009, 2011) and phthalates were shown to have an anti-androgenic activity (Christen et al., 2010).

2.2. Anode: ITO

2.2.1. Degradation/liberation processes and environmental fate

A sintered blend of indium oxide and tin oxide (ITO) is typically used as the anode in OPVs in a ratio of $\text{In}_2\text{O}_3:\text{SnO}_2$ 9:1 (wt:wt). This nanoparticulate blend is coated on the PET substrate as a thin layer.

Since it is located next to PEDOT:PSS with its hygroscopic character (Section 2.3), ITO is prone to etching by air and water (Jørgensen et al., 2008). Indium species were detected which can diffuse through the whole OPV (Krebs and Norrman, 2007). Those indium species have not been characterized so far and their contribution to OPV degradation mechanisms has not been investigated so far. To the best of our knowledge, environmental concentrations and fate aspects of ITO – especially deriving from OPVs – in the environment are largely unknown.

2.2.2. Ecotoxicity

When ITO particles suspended in water were once a week (totally 16 times) instilled intratracheally into hamsters (dosage: 6 mg kg^{-1} ; total dosage over 16 weeks: $12.4 \pm 1.2 \text{ mg per animal}$), toxic effects such as pulmonary inflammation were observed compared to control animals (Tanaka et al., 2002). Pulmonary toxic effects in rats and mice as well as carcinogenicity in rats were observed upon inhalation exposure to $0.01\text{--}100 \text{ mg m}^{-3}$ ITO for several weeks (Nagano et al., 2011a, b). Pulmonary fibrosis in a worker exposed to ITO containing aerosols for four years has been reported (Homma et al., 2005). Indium first was suggested to be responsible for the toxic effects, since it is the main component of ITO and was proven to show toxic effects in other studies, e.g. ionic indium (InCl_3) adversely effected mice fetal development (Chapin et al., 1995). But when different dust particles, namely ITO (i.e. the sintered blend (Lison et al., 2009)), its single components In_2O_3 and SnO_2 , as well as a 9:1 (wt:wt) mix of both components without sintering, were tested for their toxicity, ITO was significantly more toxic *in vivo* (rats) and *in vitro* (rat alveolar macrophages) than its single components or the blend. This leads to the conclusion that the sintered ITO blend is a pneumotoxic entity, since the intense inflammatory response as well as the strong reactive oxygen species (ROS) production were both unique to ITO particles and did even not occur with the unsintered blend. ITO particles of a size of $<50 \text{ nm}$ were exposed to the cnidaria *Hydra attenuata* ($\text{EC}_{50} = 0.1\text{--}1 \text{ mg L}^{-1}$, 96 h exposure), the green alga *Pseudokirchneriella subcapitata* ($\text{IC}_{25} = 1\text{--}10 \text{ mg L}^{-1}$, 72 h exposure) and the micro-crustacean *Thamnocephalus platyurus* ($\text{LC}_{50} = 10\text{--}100 \text{ mg L}^{-1}$, 24 h exposure) (Blaise et al., 2008). The toxicity may be restricted to the nanoparticulate form of ITO, since ITO is applied as a semiconductive surface layer on electrodes used for biological systems without adverse effects (Bayouh et al., 2008).

2.3. Electron-hole transporting layer: PEDOT:PSS

2.3.1. Degradation/liberation processes and environmental fate

As electron-hole transporting layer, a mixture of poly(3,4-ethylenedioxythiophene) and poly(styrenesulfonate) – commonly known as PEDOT:PSS – is typically used. This organic polymer is hygroscopic (Jørgensen et al., 2008), which may possibly contribute to the degradation of OPVs over time. A study investigating OPV durability with and without a layer of PEDOT:PSS indicated that the degradation of OPVs (i.e. decreasing power conversion efficiency during aging) is probably associated with water sorption to this material (Kawano et al., 2006). This hypothesis was supported by other findings. Penetrated water was detected to diffuse through all layers in OPVs and it was shown to be involved in forming non-defined particles in the PEDOT:PSS layer visible by in-depth imaging analysis (Norrman et al., 2009). Even though this structure-modifying influence of water in OPVs was shown, the observed particles were not further investigated and their contribution to OPV degradation is unknown. The exposure to an atmosphere enriched with the isotope $^{18}\text{O}_2$ indicated that the PEDOT:PSS layer is susceptible to oxidation by oxygen which penetrates into OPVs (Krebs and Norrman, 2007). Consequently, PEDOT:PSS's characteristics are suspected to contribute to decreasing power conversion efficiencies in OPVs, but possible mechanisms how it really affects the OPV performance have first to be elucidated. In order to protect the

PEDOT:PSS and other layers elongating OPV lifetime, water and oxygen scavenger substances should be included into PET barrier films.

Since PEDOT:PSS has a hydrophilic character (Döbbelin et al., 2008), it can be assumed that after potentially being released into the environment this polymer would rather partition into the water phase than into soil or biota. PEDOT:PSS is nowadays one of the most important conductive polymer used not only in photovoltaics but also for many other applications such as antistatic layers (Kirchmeyer and Reuter, 2005). To the best of our knowledge, concentrations of PEDOT:PSS upon leaching to the environment have not been determined so far and no systematic investigation data are available regarding its environmental fate.

2.3.2. Ecotoxicity

No cytotoxicity or inflammatory response was detected when PEDOT:heparin electrodes were exposed to mouse fibroblasts and human neuroblastoma compared with standard platinum controls (Asplund et al., 2009). Moreover, PSS-doped PEDOT-biosensors did not show any negative effect on proliferation and differentiation of mouse myocytes (Miriani et al., 2008) and no negative effect was observed with PEDOT-coated stainless steel electrodes on human epithelial cells (Del Valle et al., 2007). These results indicate that PEDOT is nontoxic in its polymeric form. On the other hand, particulate PEDOT materials (between 55 and 1350 nm) can cause different cytotoxic effects in human lung fibroblasts and mouse macrophages (Oh et al., 2010). Apoptosis, necrosis, and ROS production were increased in both cell lines compared to a control, with highest impact when applying the smallest particles (55 nm). Moreover, the viability (determined by the amount of ATP in the cells) was highest in cells exposed to the largest particles (1350 nm). Cytotoxic effects already detectable with a nanoparticle concentration of 10 mg L^{-1} were increasing when augmenting the concentration to 25, 100, 250, and finally 500 mg L^{-1} . These findings underline possible toxic effects of usually nontoxic substances when present in nanoparticulate form.

No information exists about toxicity of PSS itself. Besides the study mentioned above (Miriani et al., 2008), gold nanorods capped with PSS are significantly less toxic than pure gold nanorods, but still show cytotoxic effects against human gingival epithelioid and cancer cells after uptake (Parab et al., 2009). In comparison, polystyrene (PS) in nanoparticulate form are taken up by fish (medaka; *Oryzias latipes*) and are organ-distributed as well as toxic (Kashiwada, 2006), whereas they cause reduced population growth rates in rotifers (*Brachionus manjavacas*) (Snell and Hicks, 2011). Therefore, PSS in nanoparticulate form may also show a toxic effect but still needs to be investigated.

2.4. Electron-donor: P3HT

2.4.1. Degradation/liberation processes and environmental fate

Nowadays, the organic polymer poly(3-hexylthiophene-2,5-diyl) (P3HT) – as well as derivatives therefrom – is commonly used as electron-donor in the light-adsorbing layer of OPVs (Deibel et al., 2010). It was found that poly(*p*-phenylene-vinylene)-based (PPV) polymers are degraded by photo-oxidation, which were widely used for OPVs before it was demonstrated that P3HT is more efficient as OPV constituent (Cumpston and Jensen, 1995; Dam et al., 1999). In contrast to the photolysis of the PPV vinyl double bond via singlet oxygen (Jørgensen et al., 2008), P3HT appears to be degraded by a radical building process leading to alkyl side chain oxidation and sulfur oxidation, and subsequently, to the scission of the thiophene ring (Manceau et al., 2008). The sulfur atom of the thiophene ring is oxidized forming sulfoxides, sulfones and sulfinate esters (Manceau et al., 2009, 2010). Besides singlet oxygen formation also radical-based degradation mechanisms are postulated as crucial factors in the degradation of PPV-based polymers (Chambon et al., 2011; Hintz et al., 2011). Oxidative reactions in the organic polymer layer were leading to degradation effects such as diminished absorbance intensity and

decreased charge-carrier mobility, finally resulting in poor performances of P3HT-based OPVs (Chang et al., 2008). The conclusion of such investigations is that P3HT has to be properly packaged to protect it against UV, humidity and oxygen in order to diminish degradation processes. Protection can also be achieved by blending with stabilizing additives. For instance, a blend of P3HT with (6,6)-phenyl C61 butyric acid methyl ester (PCBM; Section 2.5) properly packaged (impermeable for oxygen) led to increasing durability (Rivaton et al., 2010).

Besides the attempt to elucidate P3HT degradation mechanisms, nothing is known about the fate of this organic polymer in the environment and it is unknown whether it could reach the environment in bioavailable form.

2.4.2. Ecotoxicity

No toxicity data for P3HT are available. Other plastics, such as PET (Section 2.1) can cause toxicity when disintegrating into smaller pieces. Therefore, it is also possible that P3HT nanoparticles reveal adverse effects, which still has to be examined. In order to assess the environmental impact of P3HT, its degradation products such as sulfoxides, sulfones and sulfinate esters should also be identified and tested for possible adverse effects under environmentally relevant conditions.

2.5. Electron-acceptor: PCBM

2.5.1. Degradation/liberation processes and environmental fate

The fullerene derivative (6,6)-phenyl C61 butyric acid methyl ester (PCBM) proved to be one of the best electron-acceptors leading to high power conversion efficiencies, for which reason it is the most popular acceptor in OPVs (Brabec et al., 2010). Fullerenes are widely used in different applications (e.g. as semiconductor) and are manufactured in large quantities, although they are considered to be potentially problematic for the environment when released in substantial amounts (Colvin, 2003).

Currently, fullerenes predicted environmental concentrations are low. They are estimated in Switzerland to be in the order of $0.02\text{--}0.2 \text{ ng L}^{-1}$ in surface water and $3.7\text{--}25.1 \text{ ng L}^{-1}$ in wastewater treatment plant (WWTP) effluent (Gottschalk et al., 2009). In the same study, the deposition rate into soil was determined at $0.02\text{--}0.06 \text{ ng kg}^{-1} \text{ year}^{-1}$ (all values in the range of lower Q(0.15) and upper Q(0.85) quantiles). Fullerenes can reach the environment through soot generated by combustion of different materials e.g. in incineration plants (Isaacson et al., 2009; Oberdörster et al., 2005). They are highly insoluble in water. Thus, the presence of organic solvents can have a tremendous influence on their fate, i.e. transport mechanisms or uptake by organisms. This solubility aspect can be illustrated with preparation methods for colloidal suspensions. On the one hand, fullerenes can be dissolved in an organic solvent, e.g. tetrahydrofuran (THF) with subsequent dispersion in water and subsequent removal of THF. Because of potential (eco)-toxicological risks associated with usage of chlorinated and aromatic solvents during OPV production process, water-based processes are currently under development (Andersen et al., 2011; Søndergaard et al., 2011). Without organic solvents, only prolonged stirring over weeks will disperse fullerenes in the water phase (Ma and Bouchard, 2009). It was shown that fullerenes gain hydrophilic character after being mixed with water by means of a spontaneous surface hydroxylation (Labille et al., 2009). Nevertheless, the formation of colloidal suspensions is dependent on environmental factors such as pH and ionic strength (Ma and Bouchard, 2009). Conclusively, the fate of fullerenes potentially being released into the environment has to be studied in detail for every single habitat under its specific conditions and due to their hydrophobic character they will partition into soil and biota rather than into the water phase. Furthermore, the size of fullerene aggregates is highly dependent on the presence of natural organic matter (NOM). Fullerenes tend not to aggregate to the same

Table 1

Toxic and inhibitory effects of differently prepared fullerene–water suspensions on diverse organisms.

| Organism(s) | Preparation method | Effects | Reference |
|---|--------------------|---|---|
| <i>Bacteria</i> | | | |
| Bacterial soil community | THF | No effect detected on basal respiration, microbial activity, biomass, enzymatic activity, community composition | (Tong et al., 2007) |
| Nitrate-reducing bacterial community | THF | Complete inhibition of microbial acetate oxidation | (Gao et al., 2011) |
| <i>Escherichia coli</i> | THF | MIC = 0.5–1.0 mg L ⁻¹ | (Lyon et al., 2005) |
| | SDS | MIC > 342 mg L ⁻¹ | (Xia et al., 2010) |
| | THF | No ROS-induced toxicity but membrane protein oxidation through direct contact | (Lyon and Alvarez, 2008; Lyon et al., 2008) |
| <i>Escherichia coli</i> , <i>Salmonella typhimurium</i> | Dispersants | No genotoxicity in a variety of different tests | (Shinohara et al., 2009) |
| <i>Bacillus subtilis</i> | THF | MIC = 1.5–3.0 mg L ⁻¹ | (Lyon et al., 2005) |
| | THF; PS | MIC = 0.08–0.1 mg L ⁻¹ ; MIC = 0.4–0.6 mg L ⁻¹ | (Lyon et al., 2006) |
| | SDS | MIC > 342 mg L ⁻¹ | (Xia et al., 2010) |
| | THF | Change in phospholipid composition | (Fang et al., 2007) |
| | THF | No ROS-induced toxicity but membrane protein oxidation through direct contact | (Lyon and Alvarez, 2008; Lyon et al., 2008) |
| <i>Pseudomonas putida</i> | THF | Change in phospholipid composition | (Fang et al., 2007) |
| <i>Invertebrates</i> | | | |
| Different invertebrates | PS | LC ₅₀ (96 h) > 35 ppm and LC ₅₀ (21 d) > 5 ppm, but mortality rates were increased and offspring number decreased | (Oberdörster et al., 2006) |
| <i>Daphnia magna</i> | THF; PS | LC ₅₀ (48 h) = 0.8 ppm; LC ₅₀ (48 h) > 35 ppm | (Zhu et al., 2006) |
| <i>Hydra attenuata</i> | 24 h rotating | EC ₅₀ (96 h) = 10–100 mg L ⁻¹ | (Blaise et al., 2008) |
| <i>Mytilus galloprovincialis</i> | Sonication | Extracellular lysozyme release | (Canesi et al., 2010) |
| <i>Fish</i> | | | |
| <i>Micropterus salmoides</i> | THF | Brain lipid peroxidation and gill glutathione depletion | (Oberdörster, 2004) |
| <i>Mammals</i> | | | |
| Different mammalian cell lines | THF | Severe ROS-induced toxic effect compared to no effect with C ₆₀ (OH) _n (no THF) | (Isakovic et al., 2006) |
| Human dermal fibroblasts | Various | LC ₅₀ (48 h) = 20 ppb; 1000 ppb for C3; not reached for C ₆₀ (OH) ₂₄ | (Sayes et al., 2004) |
| Human lymphocytes | Ethanol; PS | Genotoxicity above 4.2 µg L ⁻¹ ; above 2.2 µg L ⁻¹ | (Dhawan et al., 2006) |
| Hamster cells, living mice | Dispersants | No genotoxicity in a variety of different tests | (Shinohara et al., 2009) |

THF — tetrahydrofuran preparation method, Section 2.5. PS — prolonged stirring in water, Section 2.5. For other preparation methods see corresponding reference. MIC — minimal inhibitory concentration. LC₅₀ — lethal concentration for 50% of tested organisms. EC₅₀ — concentration arousing an effect in 50% of tested organisms.

extent when NOM is at hand than they do in the absence of NOM. Humic acids and fulvic acids were shown to be responsible for a size distribution shift of fullerene aggregates towards smaller sizes (Xie et al., 2008). The fate and toxicity of fullerenes in natural aquatic habitats hence depends on the presence of NOM and is presumably not the same as investigated in most of the studies under simplified laboratory conditions.

Besides these studies about solubility and aggregation, further fate aspects were discussed for fullerenes relevant under environmental conditions. It was described that the polyaromatic hydrocarbon naphthalene adsorbs to fullerene with limited desorption afterwards (Cheng et al., 2004). Like this, fullerenes can act as carriers for hydrophobic pollutants changing their partitioning pattern. For instance, it was found that the highly hydrophobic – and therefore showing low mobility – pollutants phenanthrene and 2,2',5,5'-tetrachlorinated biphenyl (PCB) show significantly enhanced mobility through sandy soil columns in the presence of fullerenes, presumably through irreversible sorption of these chemicals to C₆₀ and co-transport (Zhang et al., 2011). The mechanisms of organic compound sorption to carbon nanomaterials such as fullerenes have recently been reviewed in detail (Yang and Xing, 2010).

2.5.2. Ecotoxicity

Fullerenes have been well investigated for toxic effects (for compilation see Table 1). No effects of fullerenes on soil bacterial communities were found (Tong et al., 2007). The authors claim that in the presence of NOM, fullerenes are partly sorbed to NOM and the remaining dissolved fullerenes do not express any toxic activity. Minimal inhibitory concentrations (MIC) of 0.4 to 0.6 mg L⁻¹ were found for *Bacillus subtilis* when a C₆₀-water suspension was applied (produced by prolonged

stirring), whereas suspensions produced with the aid of THF dissolution (see above) were ten times more toxic (Lyon et al., 2006). Due to the fact that the THF-method is faster than prolonged stirring in water, a lot of toxicity studies were carried out with suspensions in which residues of THF were still present in fullerene aggregates causing (at least in part) the observed toxicity (Brant et al., 2005). Additionally, the surface of such fullerenes suspended in water by means of the THF-method is charged more negatively, which can have an influence on their fate (e.g. partition properties) and thereby on toxicity as well (Brant et al., 2005). Nevertheless, the phospholipid composition of the membranes of both *Pseudomonas putida* and *B. subtilis* was altered when exposed to C₆₀, which could be a protection mechanism against oxidative stress (Fang et al., 2007). The formation of ROS was assumed to be in charge for the toxic effects (Isakovic et al., 2006), but further studies seem to contradict this hypothesis (Lyon et al., 2008), claiming that direct contact of fullerene with the bacterial membrane is leading to the oxidation of membrane proteins (Lee et al., 2007; Lyon and Alvarez, 2008). Moreover, a C₆₀-water suspension (0.14 mg L⁻¹) can completely inhibit microbial oxidation of acetate by nitrate-reducing bacteria (Gao et al., 2011).

Fullerenes are toxic for fishes (*Micropterus salmoides*, largemouth bass). After 48 h of exposure to a 0.5 ppm C₆₀-water suspension (THF-method), they showed lipid peroxidation in their brains and a slight glutathione (GSH) depletion in their gills (Oberdörster, 2004). A THF produced C₆₀-water suspension was much more toxic (LC₅₀ = 0.8 ppm after 48 h exposure) for *Daphnia magna* (*D. magna*) than a suspension produced by means of prolonged stirring (LC₅₀ > 35 ppm after 48 h exposure) (Zhu et al., 2006). Moreover, different invertebrates were not diminished by 50% with a 35 ppm C₆₀-water suspension (prolonged stirring) even though exposed for 3 weeks (Oberdörster et al., 2006).

Furthermore, fullerene did show a toxic effect ($EC_{50} = 10\text{--}100\text{ mg L}^{-1}$, 96 h exposure) for *H. attenuata* (Blaise et al., 2008). The stability of hemocyte membrane of the bivalve *Mytilus galloprovincialis* was not affected by C_{60} -water suspensions up to a concentration of 10 mg L^{-1} (Canesi et al., 2010). Comprehensive reviews about toxic effects of fullerenes on invertebrates (Baun et al., 2008a) and fish (Handy et al., 2008a) were published as well.

C_{60} -water suspensions are toxic for human dermal fibroblasts ($LC_{50} = 20\text{ ppb}$, 48 h) (Sayes et al., 2004). Additionally, different derivatives of C_{60} with various functional groups at their surfaces did not show the same toxicity as pristine, underivatized C_{60} . For instance, derivatives such as C_3 were significantly less cytotoxic with an LC_{50} of about 1000 ppb, and $C_{60}(OH)_{24}$ was even not able to reach the LC_{50} within its range of solubility in water (Sayes et al., 2004). Conclusively, the impact of fullerenes is dependent on its surface derivatization and therefore direct transfer of cytotoxic data of C_{60} to the derivative PCBM present in OPVs is not possible. Another point which is still up for debate is the potential genotoxicity of fullerenes. Whereas studies exist which show genotoxicity of C_{60} in human lymphocytes at a concentration as low as $2.2\text{ }\mu\text{g L}^{-1}$ (Dhawan et al., 2006), others claim that C_{60} -water suspensions do not show genotoxicity (Matsuda et al., 2011; Shinohara et al., 2009). Elaborate reviews were published as well about how fullerenes can enter the human body (Oberdörster et al., 2005) and what impact nanomaterials can have on the DNA of aquatic and marine organisms (Klaine et al., 2008).

Together with the acute toxicity of fullerenes, there is additionally an indirect toxicity by means of increased bioavailability of sorbed pollutants. In toxicity tests with *P. subcapitata* and *D. magna*, pentachlorophenol (PCP) lost part of its toxic effect when C_{60} is present,

whereas phenanthrene was significantly more toxic when sorbed to fullerene (Baun et al., 2008b).

2.6. Electron transporting layer and optical spacer: ZnO and TiO_2

2.6.1. Degradation/liberation processes and environmental fate

In OPVs, ZnO nanoparticles are often used as electron transporting layer and TiO_2 nanoparticles can be assembled as optical spacer (Gilot et al., 2007; Kim et al., 2006). It was shown before that due to washout, nanoparticles (e.g. TiO_2 nanoparticles) are released from paints on outdoor facades into the environment in significant amounts over one year of testing (Kaegi et al., 2008, 2010). In that study, the runoff of a newly painted model facade ($600\text{ }\mu\text{g Ti L}^{-1}$) compared to a two-year old real facade ($450\text{ }\mu\text{g Ti L}^{-1}$) was collected and analyzed by ICP-MS and TEM. Even though approximately 98% of titanium can be removed in the biological treatment facilities of a WWTP through sorption to NOM and subsequent sedimentation, up to $20\text{ }\mu\text{g L}^{-1}$ TiO_2 nanoparticles in the range of 4 to 30 nm were still found in the WWTP effluent and can finally reach aquatic systems like rivers and lakes (Westerhoff et al., 2011).

The form and aggregation behavior of ZnO and TiO_2 nanoparticles depend on the ambient media composition. For instance, the presence of amino acids as well as acidic pH conditions is stabilizing ZnO nanoparticles in the monodisperse form (Molina et al., 2011). Furthermore, NOM can adsorb to ZnO as well as TiO_2 leading to increased negative surface charges which results in less aggregation of the nanoparticles (Zhang et al., 2009). On the other hand, the presence of divalent cations such as Ca^{2+} is leading to the aggregation of the particles due to processes such as charge neutralization, as a

Table 2

Toxic and inhibitory effects of ZnO and TiO_2 nanoparticles on diverse organisms.

| Organism(s) | Particle (diameter [nm]) | Effects | Reference |
|--|--|--|--|
| Bacteria | | | |
| Undefined bacterial soil community | ZnO (20–30); TiO_2 (15–20) | Decreased total soil respiration, decreased biomass, altered bacterial community composition ($ZnO > TiO_2$) | (Ge et al., 2011) |
| <i>Escherichia coli</i> | ZnO (30–40); TiO_2 (30–40) ZnO (20); TiO_2 (5–10) | LD_{50} (2 h) = 21.1 mg L^{-1} ; LD_{50} (2 h) = 1104.8 mg L^{-1} Damaged cell membranes after 1 h exposure to 100 and 500 mg L^{-1} | (Hu et al., 2009) (Mileyeva-Biebesheimer et al., 2010) |
| <i>Enterococcus faecium</i> | ZnO (20); TiO_2 (5–10) | No effect on cell membrane integrity | (Mileyeva-Biebesheimer et al., 2010) |
| <i>Salmonella typhimurium</i> | ZnO (30); TiO_2 (50) | Concentration-dependent internalization and weak mutagenic effect | (Kumar et al., 2011) |
| Algae | | | |
| <i>Scenedesmus</i> sp. | TiO_2 (<25) | EC_{50} (72 h) = 16.12 mg L^{-1} | (Sadiq et al., 2011) |
| <i>Chlorella</i> sp. | TiO_2 (<25) ZnO (20); TiO_2 (5–10) | EC_{50} (72 h) = 21.2 mg L^{-1} EC_{30} (6 d) = 20 mg L^{-1} ; EC_{30} (6 d) = 30 mg L^{-1} | (Sadiq et al., 2011) (Ji et al., 2011) |
| <i>Pseudokirchneriella subcapitata</i> | ZnO (30) | IC_{50} (72 h) = $68\text{ }\mu\text{g L}^{-1}$ | (Franklin et al., 2007) |
| Plants | | | |
| <i>Arabidopsis thaliana</i> | ZnO (44) | Reduced seed germination, root elongation, leave growth | (Lee et al., 2010) |
| 6 different plant species | ZnO (20) | Severe inhibition of germination rate and root growth | (Lin and Xing, 2007) |
| Invertebrates | | | |
| <i>Eisenia fetida</i> | ZnO (30) | Decreased toxicity when exposed to nanoparticles in agar than in solution | (Li et al., 2011) |
| Fish | | | |
| <i>Danio rerio</i> | ZnO (20); TiO_2 (<20) ZnO (30) TiO_2 (240–280) | LC_{50} (96 h) = 1.793 mg L^{-1} ; no toxicity LC_{50} (96 h) = 3.969 mg L^{-1} Significantly impaired reproduction after exposure to low-dose nanoparticles | (Zhu et al., 2008) (Yu et al., 2011) (Wang et al., 2011) |
| <i>Oncorhynchus mykiss</i> | TiO_2 (21) | Slight respiratory toxicity, metabolism disturbances and oxidative stress | (Federici et al., 2007) |
| Mammals | | | |
| Mouse cells | ZnO (50–70); TiO_2 (<40) | Altered cellular morphology, decreased mitochondrial function and enhanced apoptosis ($ZnO > TiO_2$) | (Jeng and Swanson, 2006) |

Mean particle diameter determined by authors or indicated by producer, agglomeration in solution not included. LD_{50} – lethal dose for 50% of tested organisms. EC_{50} – concentration arousing an effect in 50% of tested organisms. EC_{30} – concentration arousing an effect in 30% of tested organisms. IC_{50} – inhibitory concentration for 50% of tested organisms.

result of which the larger aggregates are taken up and accumulated in cells to a lesser extent (Zhang et al., 2009). Conclusively, a variety of factors such as the NOM concentration, ionic strength, pH, particle size, area and shape as well as surface charge is influencing the accumulation and bioavailability of nanoparticles and defines their fate and toxicity (Handy et al., 2008b). All these factors have as well an effect on whether nanoparticles are dedicated to sedimentation or dispersion, which has been reviewed recently (Quik et al., 2011). When sedimentation takes place, they are not available for the uptake into limnic aquatic organisms anymore, but benthic organisms are exposed since nanoparticles will accumulate in sediment. At the opposite, when nanoparticles dissolve, the dissolved substances show a completely different toxicity pattern than in particulate form (Borm et al., 2006). Whereas dissolved metals are taken up by means of ion transporters, other uptake mechanisms play a role in the case of nano-metals, e.g. endocytosis (Shaw and Handy, 2011).

Environmental concentrations of the corresponding nanoparticles are not identified properly, as a result of which they have to be determined by modeling. Predicted environmental concentrations for TiO_2 in Switzerland were $0.02\text{--}0.09\ \mu\text{g L}^{-1}$ in surface water, and $3.5\text{--}16.3\ \mu\text{g L}^{-1}$ in WWTP effluent water (Gottschalk et al., 2009). Deposition rates into soil were estimated to be $0.2\text{--}1.0\ \mu\text{g kg}^{-1}\ \text{year}^{-1}$ (all values as a range of lower $Q(0.15)$ and upper $Q(0.85)$ quantiles). The corresponding concentrations for ZnO were: $0.03\text{--}0.13\ \mu\text{g kg}^{-1}\ \text{soil year}^{-1}$ (deposition rate) and $0.01\text{--}0.06\ \mu\text{g L}^{-1}$ surface water (environmental concentration). Another study predicted similar $0.7\ \mu\text{g TiO}_2\ \text{kg}^{-1}$ in soil and significantly higher $0.4\ \mu\text{g TiO}_2\ \text{L}^{-1}$ in water, but without taking into account sedimentation processes (Mueller and Nowack, 2008). If these predicted concentrations can live up to realistic environmental concentrations, no severe direct toxic effects are to be expected in the environment, since the predicted concentrations are at least one magnitude smaller than the values determined in toxicity studies (Section 2.6.2). Even experimentally determined concentrations of TiO_2 nanoparticles of different steps in a WWTP (where TiO_2 is assumed to be concentrated) were not in the acutely toxic range (Kiser et al., 2009). Filtered samples ($0.7\ \mu\text{m}$ cut-off) contained between 14 and $66\ \mu\text{g titanium L}^{-1}$ and unfiltered samples (containing mainly particles in the micrometer range) between 35 and $8464\ \mu\text{g titanium L}^{-1}$, which is still below the EC_{50} and IC_{50} values mentioned in Section 2.6.2. Despite of this, an eye has to be kept on bioaccumulation and long-term effects of low doses.

2.6.2. Ecotoxicity

The acute toxicity of ZnO and TiO_2 nanoparticles on a wide variety of organisms is known (compilation in Table 2). The LD_{50} value for ZnO nanoparticles was $21.1\ \text{mg L}^{-1}$ (2 h exposure) in *E. coli* and $1104.8\ \text{mg L}^{-1}$ for TiO_2 nanoparticles (Hu et al., 2009). The uptake of ZnO and TiO_2 nanoparticles by *Salmonella typhimurium* was shown using flow cytometry analysis and TEM (Kumar et al., 2011) and a slight mutagenic effect on certain strains was shown by means of an AMES test. TiO_2 nanoparticles damaged cell membranes of the Gram-negative bacterium *E. coli*, whereas those of the Gram-positive bacterium *Enterococcus faecium* were not (Mileyeva-Biebesheimer et al., 2010). ZnO and TiO_2 nanoparticles have negative effects on bacterial soil communities (Ge et al., 2011). Decreasing total soil respiration and extractable DNA amount indicated a drop in bacterial biomass and the bacterial community composition (terminal restriction fragment length polymorphism (T-RFLP) analysis) was altered during incubation time. Both effects were stronger for ZnO nanoparticles.

TiO_2 nanoparticles showed EC_{50} values of $16.12\ \text{mg L}^{-1}$ in the algae *Scenedesmus* sp. and $21.2\ \text{mg L}^{-1}$ in *Chlorella* sp., nano-sized TiO_2 was almost double as toxic as micron-size bulk TiO_2 (Sadiq et al., 2011). *Arabidopsis thaliana* seed germination, root elongation and leave growth were significantly hindered when exposed to ZnO nanoparticles (Lee et al., 2010). Germination rate of corn was decreased by ZnO nanoparticles and the root growth of all tested plants (i.e. corn, cucumber, ryegrass, rape, radish and lettuce) was inhibited (Lin and Xing, 2007). More toxicity

tests were carried out with soil organisms, i.e. plants, crustaceans and insects (Manzo et al., 2011). ZnO nanoparticles affected the earthworm *Eisenia fetida* less when put in solid agar and on filter paper (simulating soil conditions) than when added dispersed in water (Li et al., 2011). Complete mortality occurred in zebrafish (*Danio rerio*) embryos and larvae exposed to ZnO nanoparticles for 96 h after fertilization at $50\ \text{mg L}^{-1}$ (Zhu et al., 2008). TiO_2 nanoparticles did not show any toxicity to *D. rerio*, whereas slight respiratory toxicity, metabolism disturbances and oxidative stress were shown in *Oncorhynchus mykiss* (rainbow trout) (Federici et al., 2007). Furthermore, reproductive disruption was shown for *D. rerio* when exposed to $0.1\ \text{mg L}^{-1}$ TiO_2 for 13 weeks (Wang et al., 2011). Toxic effects such as enhanced apoptosis were found for ZnO nanoparticles ($50\text{--}100\ \text{mg L}^{-1}$) in mouse neuroblastoma (Jeng and Swanson, 2006). Contrariwise, TiO_2 nanoparticles were significantly less toxic showing similar effects but not until applying $>200\ \text{mg L}^{-1}$.

Metallic nanoparticles are partly toxic because of their particulate form as well as of metals, which are dissolving into solution. The IC_{50} values for ZnCl_2 , bulk ZnO and nano-ZnO on the freshwater alga *P. subcapitata* after 72 h of incubation were all between 60 and $70\ \mu\text{g Zn}^{2+}\ \text{L}^{-1}$ and therefore the effect was related to dissolved zinc (Franklin et al., 2007). Toxic effects of ZnO and TiO_2 nanoparticles on the green algae *Chlorella* sp. were related to metal ions (Ji et al., 2011). Other studies were not able to properly correlate the toxicity of nanoparticles to the particulate form or metal ions illustrating that far more research is required to close this knowledge gap (Yu et al., 2011).

2.7. Cathode: aluminum

2.7.1. Degradation/liberation processes and environmental fate

Aluminum is often used as cathode in OPVs. Even though OPVs are packaged with PET, tiny amounts of oxygen and water can diffuse into the inner layers. By $^{18}\text{O}_2$ labeling, oxygen was shown to diffuse into OPVs, mainly through pinholes in the aluminum cathode (Norrman and Krebs, 2006; Norrman et al., 2006) as well as between the metal grains (Krebs and Norrman, 2007). Aluminum species dissolve into the active layer where they react with PCBM resulting in organo-aluminum species. These organo-aluminum species then react with the penetrated oxygen leading to aluminum oxide, which is an insulator and is therefore hindering proper charge carrier mobility. A similar but not identical mechanism was also found for the diffusion of water into OPVs. By means of H_2^{18}O it was shown that water is mainly penetrating OPV devices in between the aluminum cathode grains (Norrman et al., 2009). Therefore, the aluminum cathode could be an important factor for decreasing OPV power conversion efficiencies during aging, unless the PET barrier films are made completely impermeable for oxygen and water.

Aluminum is the third most common element in the earth's crust and in nature it occurs ubiquitously as water-insoluble aluminum silicates and aluminum oxides, whose bioavailability and bioactivity is negligible (Verstraeten et al., 2008). Aluminum potentially being released from OPVs would as well immediately react to aluminum oxide without posing a threat to the environment.

2.7.2. Ecotoxicity

Since aluminum is present as an elemental metal layer in OPVs (Galagan et al., 2011), its ecotoxicity is supposed to be negligible. Only in highly acidic soils aluminum occurs soluble as Al^{3+} , which can cause phytotoxic (Jiang et al., 2008) or as well neurotoxic effects (Verstraeten et al., 2008). Aluminum nanoparticles are up for discussion concerning fate and ecotoxicity (Darlington et al., 2009), but are not present in OPVs.

3. Scenarios leading to potential leaching of OPV components

Until today, no policy as well as no methods and processes exist in order to recycle OPVs. However, since precious (e.g. Ti) and rare earth

metals (e.g. In) are contained in OPVs, the development of an appropriate recycling method will be driven by the incentive of recovering at least these metals (Virolainen et al., 2011), especially when produced in large-scale. However, recycling may require organic solvents to separate single OPV components, which might themselves be of environmental concern. These contrasting concerns should be evaluated carefully on comparative basis. Nevertheless, without recycling, disused OPVs can face the following end-of-life scenarios: “proper” disposal via incineration (energy recovery), controlled landfilling, and preservation until a recycling method is developed, as well as “inadequate” disposal via uncontrolled open burning, uncontrolled landfilling, and distribution from landfilling into aquatic systems (Al-Salem et al., 2009; Lazarevic et al., 2010). Especially where disposal infrastructure is not yet established, as often the case in developing countries, OPV-based products such as lamps (Krebs et al., 2010, 2011) might encounter improper disposal.

If not incinerated, OPVs are exposed to harsh environmental conditions and different factors influence the continuous weathering of the materials in their end-of-life phase as well as during use (Fig. 2). One major aspect is UV radiation, which can cause photooxidation (Chambon et al., 2011; Manceau et al., 2009) and yellowing of organic polymers such as P3HT (Section 2.4) with a possible release of OPV components due to this aging process. Moreover, since the plastic packaging of such OPVs is not entirely impermeable for oxygen and water, ambient humidity (surface water, rain, fog) and oxygen can penetrate the OPVs in minute concentrations (Krebs and Norrman, 2007; Norrman et al., 2009), leading to undesirable reactions in the ITO (Section 2.2), PEDOT:PSS (Section 2.3), and aluminum layers (Section 2.7). Mechanical stress during use, on a landfill site or when distributed into water systems can result in deterioration of the OPVs, increasing permeability for humidity and oxygen. Once mechanically damaged or even disintegrated to small pieces (Eriksson and Burton, 2003) with a large inner surface exposed to ambient conditions, certain components can be prone to washout: especially nanoparticles like PCBM (Section 2.5), ZnO and TiO₂ (Section 2.6) can possibly be washed out in nanoparticulate form or as aggregates (Kaegi et al., 2008, 2010) and be found afterwards in surface waters (Westerhoff et al., 2011). Another factor that may accelerate OPV aging and therefore the release as well of OPV components is temperature. Directly exposed to the sun, temperatures can possibly rise above the glass temperature of PET (72 °C, Section 2.1) (Sinha et al., 2010), as a result of which these plastics are more permeable for oxygen and water (Yasuda and Hirotsu, 1977). Conclusively, there is a wide variety of factors which could have a detrimental effect on OPV structure potentially leading to cell weathering, aging, degradation and possible release of compounds into the environment when inconsiderately disposed.

When incinerated, attention has to be paid that it happens in official incineration plants and not in open fires due to toxic emissions. When PET is incinerated, a variety of toxic substances were found in the airborne soot as well as residue ash, e.g. different heavy metals and polycyclic aromatic hydrocarbons (Estrellan and Iino, 2010). Furthermore, fullerenes occur in soot generated from combustion of a variety of materials (Isaacson et al., 2009). Therefore, fullerenes present in OPVs (PCBM, Section 2.5) may potentially be released into the air when OPVs are incinerated. It also has to be considered how to dispose the residue ashes in an environmentally friendly way.

4. Discussion

The manifold application possibilities and advantages of OPVs compared to traditional energy-delivering systems – especially silicon solar cells – are beyond controversy. However, it is particularly crucial to assess possible negative environmental impacts when OPVs are applied in large-scale in near future. Besides high power conversion efficiencies, the most important characteristic of OPVs is their stability against environmental factors in order to maintain its performance, exhibit long lifetimes and avoid release of its components. On the one

hand, P3HT:PCBM based bulk-heterojunction solar cells have been shown to be satisfyingly stable in accelerated aging experiments as well as under exposure to outdoor conditions for short lifespans of about a year (Hauch et al., 2008). On the other hand, when it comes to long-term usage the major drawback of OPVs is their instability against different degradation processes. These processes are derived from various factors such as oxygen, temperature, moisture, light and mechanical stress (Jørgensen et al., 2008; Manceau et al., 2011).

In the typical OPV example discussed in this review, different organic polymers are present (Fig. 1). Even though certain plastics are biodegradable (Shah et al., 2008), and first attempts were undertaken in order to develop partly biodegradable OPVs (Strange et al., 2008), the problem of plastic waste not only deriving from OPVs is far from solved. PET, PEDOT:PSS, and P3HT are all considered not to be biodegradable, which is advantageous for OPV persistence but problematic when reaching the environment. Since PET as barrier layer is the major component (from a weight perspective) of OPVs, its fate and ecotoxicity is of importance. Elaborate research has been carried out already and serious concerns have been raised because of the vast amount of non-recycled PET in the waste stream (Reis and Carneiro, 2012). Life-cycle assessments comparing PET with novel developed bioplastics such as polylactic acid (Gironi and Piemonte, 2011) and poly-beta-hydroxybutyric acid (Harding et al., 2007) revealed better performance of the bioplastics, but they do not reach the mechanic stability of PET. Concerning biodegradability of PEDOT:PSS, literature can be found about polystyrene but not about PSS or PEDOT (Chandra and Rustgi, 1998; Parker et al., 2011). Degradation mechanisms for P3HT have been investigated since it is particularly crucial to know them in order to manufacture OPVs with an extended lifetime. Nevertheless, degradation mechanisms occurring in nature are unknown. Besides (bio-)degradation studies, little is known about fate and ecotoxicity aspects of the organic polymers used here. Preliminary toxicity data of these polymers would become more meaningful as soon as it is known in which concentrations and form these polymers (and their degradation products) could reach the environment and whether they are partitioning into air, soil, water or biota. Especially, when chemically or mechanically decomposed into nanoparticles or mono-/oligomers, the fate of these components can be different from bulk material.

In the typical OPV example discussed here, ITO, PCBM, ZnO, and TiO₂ nanoparticles are used. The role of nanoparticles in wastewater and wastewater sludge has been discussed extensively (Brar et al., 2010; Kiser et al., 2009; Musee, 2010; Westerhoff et al., 2011). The problems concerning nanowaste treatment are still unsolved (Musee, 2010). There is an almost complete lack of fate and toxicity data about ITO even though it is commonly used in electronic industries (Tanaka et al., 2010). Should ITO be detected to be released from OPVs and other products in significant concentrations under environmental conditions, it would be noteworthy to determine environmental concentrations,

Table 3
Maximal amount of each OPV component produced and disposed yearly.

| OPV component | Layer thickness [nm] ^a | Mass per m ² [g] ^b | Mass per 400 km ² [t] |
|----------------------------|-----------------------------------|--|----------------------------------|
| PET (front and back layer) | 175,000 (2×) | 245 (2×) | 98,000 (2×) |
| ITO | 120 | 0.8544 | 341.8 |
| PEDOT:PSS | 40 | 0.0400 | 16.0 |
| P3HT (1:1 blend with PCBM) | 220 (0.5×) | 0.1265 | 50.6 |
| PCBM (1:1 blend with P3HT) | 220 (0.5×) | 0.1375 | 55.0 |
| ZnO | 39 | 0.2188 | 87.5 |
| TiO ₂ | 30 | 0.1272 | 50.9 |
| Al | 100 | 0.2700 | 108.0 |

^a Layer thickness values: PET (Krebs et al., 2009); ITO, PEDOT:PSS, PCBM, P3HT, Al (Galagan et al., 2011); ZnO (Gilot et al., 2007); and TiO₂ (Kim et al., 2006).

^b Assumptions for calculation: see Section 4.

released forms as well as partitioning pathways. The investigation of fullerenes has been much more comprehensive so far, even though the findings should not necessarily be directly transferred to derivatives like PCBM. Whereas data is available about acute ecotoxicity, fate issues have only been scarcely investigated. Even though studies exist about environmental concentrations, behavior in the presence of NOM, and the role as pollutant carrier, further research is necessary in order to reliably assess the fate of fullerenes in the environment. ZnO and TiO₂ nanoparticles are as well systematically studied concerning toxicity but not as much for fate issues such as leaching concentrations, forms and partitioning pathways. Modeling might help to meet such challenges. It has recently been shown that the toxicity of diverse nanoparticles on *E. coli* may be predicted by means of a nano-QSAR (quantitative structure–activity relationship) model (Puzyn et al., 2011). Perhaps such approaches will also be able to be adapted for fate predictions, simplifying experimental designs for fate research as well as the interpretation of such data.

An estimation of the maximal amounts of OPV components produced, disposed and possibly reaching the environment is calculated in this review with a few assumptions (Table 3). Given OPV modules with a life-time of one year (Hauch et al., 2008) and an approximated power conversion efficiency of 10% (National Renewable Energy Laboratory, NREL, 2012), 100 Wp (watt peak; nominal power under standardized test conditions: AM1.5 illumination, 25 °C cell temperature, 1000 W m^{−2} radiation) of power is produced by 1 m² of OPVs. Taking 1000 h of peak power of the sun per year, 400 km² of OPV area are needed in order to replace 100% of the 40 GW power produced by photovoltaics in a year (Renewable Energy Policy Network for the 21st Century, REN21, 2011). In this “worst-case scenario” for the environment, almost 200,000 tons of PET waste would be produced every year. Compared to 9.5 million tons produced worldwide in total (Reis and Carneiro, 2012), PET derived from OPVs would only contribute about 2%. 87.5 tons of ZnO nanoparticles would contribute less than 0.1% to the worldwide produced 100,000 tons (Klingshirm, 2007). Whereas estimates of the worldwide produced TiO₂ amount range from 5000 (Mueller and Nowack, 2008) to 4 million tons (Robichaud et al., 2009), 50.9 tons in OPVs would contribute between about 1 and 0.001% to the total amount. Other components (16 tons PEDOT:PSS, 50.6 tons P3HT, 55 tons PCBM, 108 tons Al) are not thought to be major contributors to worldwide production volumes as well. ITO has to be seen as an exception: 342 tons of ITO including about 148 tons of indium would be about 25% of the total 568 tons of indium produced worldwide in 2008, which was mainly used for LCD screens (Virolainen et al., 2011). Therefore, since indium is one of the critical raw materials because of its global scarcity (European Commission, 2010), as long as ITO is used for OPV production, a scale-up into the range of an annual production of 40 gigawatts peak (GWp) would pose major challenges. Due to the fact that indium used for ITO is on the one hand a rare element and on the other hand ITO represents the main contributor to the production energy of an OPV module (Espinosa et al., 2011b), great efforts are currently under way to replace ITO with alternative transparent conductors (Galagan et al., 2011; Kim et al., 2012; Krebs, 2009), which may perform better in environmental and economic assessments (Emmott et al., 2012).

5. Conclusions

For the first time, a typical OPV example was discussed layer by layer in order to identify existing knowledge gaps concerning the potential environmental impact of its components. Whereas intact solar cells during their use phase are not considered to be problematic, at the end of their life some issues have to be raised concerning leaching of substances during disposal and proper recycling methods need to be developed. Comprehensive research has been done about toxicity of nanoparticles, but there is an almost complete lack of information about environmental

concentrations and fate of all OPV components including nanoparticles and organic polymers. So far, there is no evidence for a worrying threat coming from OPVs, but environmentally relevant laboratory fate studies are advisable in order to gain insight into the behavior and effects of this cutting-edge product in complex matrices like living organisms, surface water, soil and air. End-of-life scenarios, especially recycling, should be addressed when launching a possible future large-scale production.

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