Toxicity of organometal halide perovskite solar cells

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In the last few years, the advent of metal halide perovskite solar cells has revolutionized the prospects of next-generation photovoltaics. As this technology is maturing at an exceptional rate, research on its environmental impact is becoming increasingly relevant.

erovskites are a class of crystalline compounds described by the generic chemical formula ABX3. Within this family, organometal halide perovskites (OHPs, with $A=CH_3NH_3^+$, $HC(NH_2)_2^+$ and/or Cs+; B=Pb and/or Sn; X=I and/or Br) have garnered much interest as efficient light harvesters, but also in applications such as light-emitting diodes, lasers and photodetectors, in view of their favourable intrinsic properties, such as ambipolarity, high charge-carrier mobilities, high diffusion lengths and high absorption coefficients¹. Brisk and impressive achievements have brought perovskite solar cells to a level near silicon photovoltaics in terms of efficiency (at least on a laboratory scale)², yet an important downside of these materials in their current form is that they contain heavy metals. The photovoltaic community is very much aware of the toxicity issues associated with the Pb content of highly performing perovskite solar cells, and of the strain this imposes on the public perception and acceptance of the technology³⁻⁶. Sn is being proposed as a more environmentally friendly alternative to Pb, yet it can likewise induce detrimental environmental and health effects^{7,8}. Even though the metal content per square metre of a solar panel is only a few hundred milligrams, the potential occupational and non-occupational exposure associated with the large-scale implementation of the technology should be treated with caution. In addition, upon moderate exposure to external stimuli (such as humidity, oxygen, elevated temperature or a combination of these factors) these perovskites tend to degrade into harmful compounds carrying heavy metals, which may readily leach into the environment as a result of the structural failure of a photovoltaic module⁹⁻¹¹. Based on these concerns, there is an acute need to assess the impact of the widespread application of perovskite solar technology

on the environment as well as on human and animal health. Until a clear consensus on this issue is reached — or an alternative non-toxic and equally performing perovskite compound is found — the safe deployment of this technology relies entirely on adopting precautionary measures against contamination at each stage of the device's life, from fabrication to disposal/recycling.

Revisiting the CdTe debate

The concerns raised on the large-scale use of perovskite photovoltaics in view of the presence of heavy metals are reminiscent of the debate on cadmium telluride (CdTe) solar cells, whose efficiency became industrially relevant in the 1990s. In parallel with the rising interest towards the performance of this technology, awareness of the toxicity associated with Cd (and to a lesser extent Te) also grew in the scientific community¹². The inherent toxicity of CdTe was initially assessed by extrapolating data from other Cd compounds (the socalled read-across approach), yet it later appeared evident that this method leads to incorrect conclusions and to a large uncertainty in the evaluation of toxicity¹³. An important aspect neglected in practising read-across is that the hazard associated to different compounds deriving from the same elements strongly depends on their solubility. CdTe is a thermally and chemically very stable compound with a low solubility constant, $K_{\rm sp}$, of 10^{-34} and, accordingly, its toxicity was revealed to be extremely low (particularly when compared to pure Cd and Te) once experiments not flawed by the read-across method were performed¹³. In contrast, the OHPs now used in photovoltaics are very unstable. Having a $K_{\rm sp}$ up to 29 orders of magnitude higher compared to CdTe, they can easily degrade to Pb or Sn compounds, thus significantly increasing their potential bioavailability14 and their hazard for animal and human

health, as confirmed by recent toxicity tests [Au:OK?] (see below [Au: please could you be more specific? E.g. a section/Figure/Box])^{8,15}. In order to fully evaluate such risks, specific toxicity assessments of those Pb- and Sn-based compounds that are relevant to the fabrication, degradation and decommissioning of these solar cells are necessary.

It is important to mention that, even though the actual toxicological hazard presented by CdTe is very low, rigorous industrial hygiene programmes have been implemented to protect workers' health in manufacturing facilities¹⁶. Moreover, cost-effective and environmentally friendly recycling programs have been put in place, certainly contributing to the public acceptance of CdTe-based solar cells. For instance, the company First Solar is committed to recycling every CdTe module they have produced once it reaches the end of its functional lifetime17. Considering the prospect of a degree of toxicity that exceeds that of CdTe, even stricter measures should be taken in terms of safe handling during fabrication and recycling if perovskite technology is to mature towards large-scale implementation.

Kinetics of Pb and Sn intoxication

Here, a summary is provided of how Pb and Sn from OHPs could enter the human body and how these elements are processed. In case of Pb, the contents of this section are condensed into a scheme (Fig. 1) for clarity. No scheme is reported for Sn, as the data available in the literature are currently not sufficient to provide a comprehensive picture.

Upon accidental contact with Pb-containing chemicals, three routes of intake need to be considered: gastrointestinal, respiratory and dermal uptake^{3,18}. In general, when Pb compounds enter the body, their kinetics of metabolization fit a

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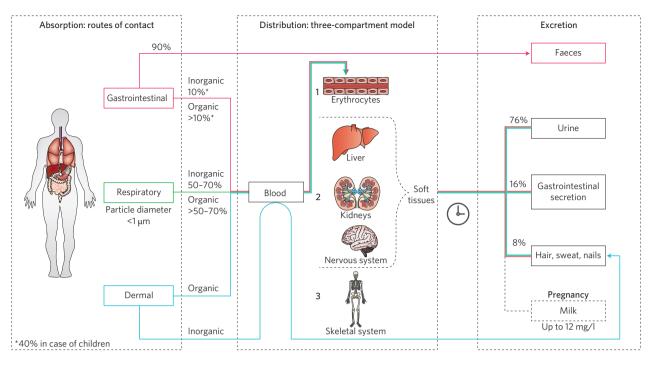


Figure 1 | Schematic overview of absorption, distribution and excretion of Pb compounds in the human body, compiled from references 3,4,18–21. For each route of intake, a percentage indicates the overall amount that can be absorbed. Pb not absorbed upon gastrointestinal intake leaves the body via the faeces (as indicated); Pb not absorbed by respiratory or dermal routes is assumed to have left the body directly by exhalation or to have lost contact through natural body movement, respectively (not indicated in the figure). Pb resides in all of the three compartments with a certain organ-specific retention time, after which it is excreted from the body. [Au: 'K_m in fat and H₂O' and Gastic acid K_m' have been deleted as their meaning was unclear, OK? If not, please provide more details.]

so-called three-compartment model^{3,19,20} (Fig. 1). Regardless of the mode of intake, blood (compartment one) transports the Pb compounds throughout the body to soft tissues (liver, kidney, nervous tissue; compartment two). Eventually, the skeleton is the major depository for Pb in the body (compartment three), with a total body burden of 90% and long half-life of 20 to 30 years (compared to only a few weeks in the former compartments)^{19–21}. Within all compartments, Pb ions cause damage through mimicry of essential elements such as Ca, Zn, and Fe21. In soft tissues, this results in impaired functionality of enzymes and receptors, whereas in blood it interferes with haem activity. During the early stages of exposure, Pb is only loosely deposited in the bones, hence some equilibration between Pb contained in the skeleton and in the blood does occur. However, upon prolonged continuous exposure Pb gradually fixates [Au: 'attaches' or 'adheres'?] to the bones as insoluble lead phosphate. Pb is finally evacuated by the excretion mechanisms of the body, including through breast milk²¹. This represents a major risk for breastfed infants, who are more susceptible to heavy metal intoxication during the early stages of development²².

The toxicity of Sn from perovskites is rather complex compared to its Pb

counterpart7. Due to the low redox potential (-0.15V) of Sn(II)/ [Au:OK to replace with 'and'?'' is slightly ambiguous.] Sn(IV) and the reducing character of Sn(II), rapid oxidation to more stable Sn(IV) occurs in ambient atmosphere. This reaction is further accelerated in aqueous environments and leads to the formation of hydroiodic acid as an acidic by-product8. Synthesis of Sn-based perovskites in laboratories typically occurs in a low-oxygen and dry environment, hence conversion to Sn(IV) in these conditions is slowed down. As a consequence, operators may be exposed to both Sn(IV) and unconverted Sn(II). This is an important factor because the difference in oxidation state has been proven to influence the net gastrointestinal absorption of Sn, and both oxidation states are not readily interconverted during transport through the body^{23,24}. For chronic exposure, the oral absorption of Sn(II) is inversely proportional to the dose of administration (within certain boundaries), whereas it does not exceed 5% (a value much lower than for the Pb counterpart) during shorter timeframes^{23,25}. In comparison, the acute oral absorption of Sn(IV) is below 1%23.

Upon ingestion of Sn compounds, some inhalation might also occur. Organic compounds can pass easily from the respiratory system to the bloodstream due to their solubility in fat, whereas inorganic

Sn compounds are more bound to pass [Au: 'likely to pass'? please clarify 'more bound to pass'], when sufficiently small in diameter and water-soluble26. So far, data on the average portion of uptake via this route are lacking but, according to physiologically based pharmacokinetic (PBPK) modelling, 70% of inhaled inorganic Sn compounds that are small enough to be inhaled at the level of the alveoli can be transported to the blood, from where they are further distributed²⁷. No data are available on the absorption through dermal contact either, although reduced penetration is expected given the low water- and fat-solubility of inorganic Sn compounds associated with perovskites. As with Pb, the absorbed Sn is distributed via systemic transport. Most researchers agree that the skeletal site is a major depository for Sn^{23,28,29} but its fate in soft tissues is still unclear^{7,29}. This holds true for the passage of Sn compounds through the blood-brain barrier as well^{7,23}. According to the PBPK model, the following rough estimation of distribution can be given: from the maximum amount of Sn absorbed (5%), 50% is distributed to excreta (specific route not mentioned), 35% is deposited in bone and 15% is uniformly distributed to remaining soft tissues³⁰. Moreover, 95% of the ingested Sn is immediately removed from the body via the faeces, and the remaining 5% is

eliminated within 400 days³⁰. Similarly to Pb, Sn(II) will interfere on a molecular level by mimicry of other divalent elements such as Ca, Fe, Zn but also Cu. Molecular deregulation has also been observed for Sn(IV), although to a much lesser extent.

Thresholds, symptoms and treatment.

For both Sn and Pb exposure, various toxicological thresholds have been indicated [Au: introduced/discussed?] over the past decades. In 2003, a maximum blood Pb level (BLL) of 5 µg/dl was imposed by the World Health Organization (WHO)⁵. Technically speaking, this is commensurate with an acute intake of only 2.5 mg of PbI₂ via ingestion or 0.5 mg via inhalation. This tolerance was however revoked in 2010 after the discovery of decreased intelligence and behavioural difficulties in children exposed to even lower values⁶. Neurological deficiencies, however, can also occur in adults, either due to chronic exposure or to a high acute uptake^{3-6,19,20,22,31}. For these cases it has also firmly been proven that genotoxicity, carcinogenicity and reproductive defects can occur along with renal and hepatic dysfunction³⁻⁶. Nausea, vomiting, abdominal pain along with headaches, seizures and muscle weakness are instead symptoms signalling moderately acute toxicity³⁻⁶. In the case of Sn, a daily tolerable intake of 2 mg/kg body weight was established by The Joint Expert Committee on Food Additives (JECFA) from the Food and Agriculture Organization of the United Nations (FAO) and WHO in 200132. Yet, JECFA concluded in 2005 that the available data so far were inadequate to establish an acute reference dose for inorganic Sn, as it was found that the concentration and the chemical nature of the compounds, rather than their dose, have a significant influence on the overall effect³³. Compared to Pb poisoning, Sn poisoning from inorganic compounds is less documented, but it has been established that the short-term effects include ataxia, muscle weakness and irritation of gastrointestinal mucosa that might lead to vomiting and diarrhoea^{7,23-25} [Au:OK?]. Upon chronic exposure, effects similar to Pb exposure are expected, such as mineral imbalance and renal and hepatic dysfunction^{7,23-25}. Effects on the reproductive and neuronal system, and the possibility of genotoxicity and carcinogenicity are still under debate⁷.

If inadvertent Pb or Sn intoxication would occur, treatment is possible. The cornerstone of metal toxicity management is naturally the termination of exposure, but in severe cases therapy in the form of chelation — administration of chemical agents, such as dimercaptosuccinic acid, that bind to and remove heavy metals from the body —

Toxicity of metal salts for precursors influenced by solubility in water and fat dermal and oral uptake exacerbated by solvent DMSO increases cell membrane permeability.

Perovskite-dedicated protocols in labs and production facilities

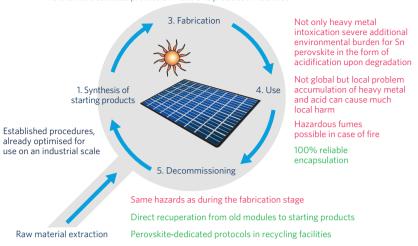


Figure 2 | Concise schematic of the life cycle of perovskite solar cells, indicating the most important hazards (red) and strategies for their control (green). Safety protocols for phases one and two have already been established and are not described here [Au: changes have been made to the caption and figure by the editor. Please check and confirm whether these are ok.]

can be initiated. Public health actions are typically initiated at 5 $\mu g/dl^{31}$. Medical treatment is advised starting from values of $45\mu g/dl^{31}$. Due to the low occurrence of Sn poisoning originating from inorganic Sn compounds, no such directive is in place.

Assessing the perovskite life cycle

Several life cycle assessments (LCAs) and similar studies on perovskite solar technology have been reported³⁴⁻³⁷. The intention of an LCA is to evaluate environmental impacts and energy balance in every stage of a product's life. Typically, five stages are considered: (1) raw material extraction, (2) synthesis of starting products, (3) fabrication, (4) use and (5) decommissioning. Inventories that contain relevant properties of all involved components are assembled and fed into specialized software that quantifies environmental impacts by returning scores in terms of so-called impact indicators. It should be noticed that, although such studies are commonly used to investigate the environmental justifiability of a new technology, their outcome may differ significantly, depending on the emphasis given to each stage of the life cycle and, probably, on the employed impact indicator³⁴⁻³⁷. Within the available studies, specific toxicity aspects related to the heavy metals used in hybrid perovskites have not been exhaustively discussed. We provide here a very concise and, above all, qualitative assessment of the toxicity of the perovskite layer in solar cells, following the typical stages of an LCA. As the starting products

for perovskite solar cells are chemicals that are already being used on an industrial scale for other applications, we assume that the corresponding material extraction and synthesis have already been optimized in terms of health and safety, and focus therefore exclusively on stages three to five of the life cycle (as concisely summarized in Fig. 2).

Fabrication. The main sources of intoxication hazard during the fabrication of OHP layers are related to the starting compounds and solvents (if required in the synthesis procedure adopted) used. The chemical nature of a compound — be it organic or inorganic — can have a major influence on the bioavailability and rate of uptake, as follows from the correlation with its solubility in fat and water (which is a proxy for how easily it can be absorbed). Consequently, the overall burden of organolead and organotin compounds is considered much higher compared to their inorganic counterparts as they can readily pass biological barriers to reach vital areas due to their relatively high fat solubility. As indicated in Fig. 1 (for the Pb case), the general absorption is significantly higher, especially via the dermal and respiratory routes^{26,38}. The commonly used sources of heavy metal intoxication upon preparation (and to some extent degradation) of Pband Sn-based perovskites can be ordered in terms of water solubility as: SnBr₂ > $SnCl_2 > Pb(NO_3)_2 > Pb(CH_3COO)_2 >$ $Pb(OH)_2 > PbCl_2 > PbBr_2 > PbI_2 > SnI_4$ > SnI₂ > SnO₂ (no data are available for

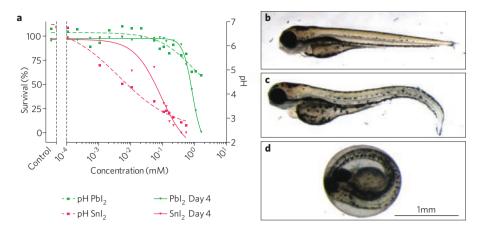


Figure 3 [Exposure to Snl_2 is much more acutely toxic to zebrafish than exposure to Pbl_2 , which correlates directly with the pH of the growth medium⁸. **a**, The survival of zebrafish 4 days post-fertilization as a function of toxicant concentration and pH. **b**, Healthy zebrafish (control). **c**, Zebrafish exposed to Pbl_2 (1.08·10⁻² mM), showing a brain haemovascular defect, heart oedema and dorsal curvature. **d**, Zebrafish embryo exposed to Snl_2 (1.62·10⁻¹ mM) showing failed hatching at 96 hours post-fertilization. Images adapted from ref. 8, NPG.

Pb(OH)I and SnCl₄). All of these are at best sparingly [Au minimally?] soluble in fat, with the exception of Pb(CH₃COO), which is soluble in both water and fat, and can thus be considered particularly hazardous. Additionally, intoxication by these chemicals can be significantly exacerbated by the presence of the commonly used solvents dimethylformamide (DMF) and dimethylsulfoxide (DMSO). Not only are these solvents toxic themselves (in particular DMF), but both are also miscible with water in all ratios, thus increasing the bioavailability and the risk of absorption by oral ingestion and via dermal contact. The hazard is even more pronounced in the case of DMSO, as this solvent increases the cell membrane permeability³⁹. Considering the above, sufficient protection in the form of gloves (minimum 15 mil latex), dust masks and glasses, as well as safe storage of waste products, represent good laboratory practice, which is critical to guarantee a safe lab or production environment. Despite being very advisable, so far perovskitededicated measures are generally not imposed in research labs, in particular where different research lines run concurrently. In large-scale production facilities, many processes can of course be automated and shielded, reducing the workers' immediate proximity to the toxicants.

Use. During their useful lifetime (stage four), the structural integrity of perovskite modules placed in uncontrolled conditions (such as on a rooftop) can be affected, which poses an immediate danger related to perovskite degradation and leakage of toxic chemicals into the immediate surroundings. Perovskite

degradation generally entails the reversion to its starting products, which then can decompose further. For the current typical perovskite solar cells, this would result in the production of PbI₂ (or PbBr₂), a small amount of metallic Pb and carbonated moieties that ultimately convert into hydroiodic acid (HI) and methylamine¹¹. In the case of Sn-based perovskites, so far SnI₂ and SnI₄ have been identified⁸. Despite recent estimations pointing out that the annual amount of spilled Pb from defective perovskite solar cells would be orders of magnitude smaller than that from emissions by other energy-related activities, a more careful toxicological investigation is highly preferable because of the danger related to local toxicant accumulation⁴⁰ [Au:OK?]. In a simplified stationary picture, it has been argued that the Pb species released during the degradation of perovskite by rain would strongly adsorb on soil particles and thereby remain concentrated in the top few centimetres (inducing a higher Pb concentration but also facilitating removal)14. Yet, this mechanism highly depends on soil composition and acidity41; thus, since an acidifier (HI) is also released upon perovskite degradation⁸, the assumption that soil may be able to immobilize Pb should be approached with great circumspection. In a worst-case scenario, the degradation products could be transported by soil water and eventually accumulate in unpredictable locations, and the concurrent increase of the environmental acidity may facilitate further dissolution of the deposited metal ions and halides⁴². Using zebrafish as a model organism, and following the guidelines from the Organisation for Economic Co-operation and Development

(OECD) for the testing of chemicals, we have established that in the case of Sn perovskites, acidification is the decisive factor of toxicity (see Fig. 3a). The transformation of SnI₂ into insoluble oxides largely nullifies direct Sn exposure to the organism, but generates HI as a by-product that, in terms of overall lethality, makes Sn-containing perovskites more acutely toxic than Pbcontaining perovskites. Yet, Pb compounds also caused multiple morphological defects in the zebrafish embryos, such as brain haemovascular defects and heart oedema (indicated in Fig. 3b). As the zebrafish genome shows overlap with 70% of protein-coding human genes and 85% of genes associated with human disease, these results also represent a first indication regarding the possible implications of human exposure⁴³. Nevertheless, studies on higher model organisms are necessary to reach a more precise consensus on the effect of these heavy-metal compounds on humans, expanding upon the basic knowledge outlined in the section 'Kinetics of Pb and Sn intoxication'. Lastly, a potentially exacerbating factor in module failure is fire, with the emission of toxic fumes. The inherent danger of such airborne toxicants is especially high because they can spread extremely quickly and are easily absorbed via inhalation. Therefore, a thorough investigation on the potential for liberating Pb or Sn, as well as the corresponding heavy-metal-containing fumes, in the event of fire is indispensable for the success of perovskite technology.

Decommissioning. According to the International Lead Association, Pb is one of the most effectively recycled materials in the world. 80% of modern Pb usage goes into the production of batteries, which are recycled according to well-established procedures. It has recently been demonstrated that waste Pb from batteries can be recycled to produce PbI₂ with high purity for use in perovskite solar cells44. At the end of their useful life. PbI₂ can be recuperated directly from the solar cells by using an appropriate solvent, purified and reused for the same purpose. As the same hazards apply here as in the fabrication stage, similar precautions are required. Such recycling programmes could be hosted by the companies themselves that commercialize perovskite photovoltaics, but the activity could also be supported by companies that have specific expertise in dealing with heavy-metal waste. In any case, these recycling programmes should be at least as environmentally friendly and costeffective as those for existing technologies (in the order of US\$0.04 W⁻¹ (CdTe) to US\$0.13 W⁻¹ (Si) or lower)⁴⁵ [Au: please confirm US dollars used here?].

Prevention through encapsulation

Considering the intoxication hazard inherent to the current OHPs, effective precautionary measures against the liberation of Pb compounds from a perovskite module are imperative. Fortunately, the common encapsulation layers used to safeguard a solar module from water and moisture also work in the opposite direction, preventing the module contents to spill into the environment. The typical (tempered) glass-glass encapsulation with ethyl vinyl acetate encapsulant (or similar) and polyisobutylene edge seal (or similar), already used in commercialized photovoltaic technologies, is likely to also prove effective for perovskite solar cells. Even if such encapsulated perovskite modules were to be damaged beyond their breaking point (for instance by hail or during an earthquake), the tough and resilient encapsulant would still encompass the active layer and would provide initial protection until they could be removed by a specialist. In addition, in case the encapsulation were to become locally defective, a simple builtin electronic test would quickly reveal degradation before it could cause harm by leakage. Nevertheless, further protection could be offered, for example by an additional 'monolithic' encapsulation, such as alumina, grown directly on top of the device stack (by atomic layer deposition)⁴⁶. Alternatively, self-healing materials may be considered (with the boundary condition of sufficient transparency) in a standalone configuration or complementary to conventional encapsulation⁴⁷. Such materials spontaneously restore damage upon cracking or ballistic puncture, helping to keep possible toxicants contained. As an auxiliary safeguard, a sufficient density of heavy-metal-capturing molecules could be incorporated into the module to confine these toxicants to an even greater extent⁴⁸. Sulfides that react with the perovskites' degradation products to form insoluble (thus inert) compounds offer another viable approach¹⁴. Similarly, to counteract the acidification that follows from HI formation during perovskite degradation, limestone powder can be incorporated into the module. However, the actual efficacy of these strategies needs to be verified by rigorous experimentation, and the costeffectiveness of more advanced encapsulation on a module level also needs to be evaluated.

Conclusions and outlook

Based on the currently incomplete knowledge of the toxicology of OHPs, there is one strict condition on which the largescale implementation of this photovoltaic technology hinges: 100% reliable containment of degradation products from modules that lose their structural integrity during their

useful life. The perovskite technology can be deployed in a completely safe way (both for human health and the environment) only if modules are fitted with an absolutely fail-safe encapsulation, resistant to extreme conditions. At the same time, LCAs need to be expanded by incorporating the possibility of module failure to accurately map the full environmental impact of OHPs in a worstcase scenario. Standardized protocols for module recycling should also be established. Furthermore, given the limited knowledge on the toxicity of the various Pb and Sn compounds and the read-across issue, more in-depth investigation is becoming very relevant in that area as well.

Pb has been playing a major role in perovskite solar cells, leading to remarkable advances in terms of efficiency and, to some extent, stability49. It is thus conceivable that Pb-based OHP technology will be the first to enter the market, on the strict condition of fail-safe encapsulation. In parallel, arguably the advances with the greatest impact could arise from anion and cation exchange in the perovskite crystal by suitable stable alternatives. Herein, Pb or Sn could either still be present in a more rigid perovskite matrix, or replaced by another (preferably non-toxic) metal, such as Bi⁵⁰. In any case, the challenge then lies in the retention of favourable properties in terms of bandgap, absorption coefficient, charge transport and ease of processing. As such, future avenues of perovskite research to achieve intrinsic environmental friendliness will undoubtedly stem from the interplay between theoretical simulations and experimental discoveries [Au:OK?].

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