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## Absorption spectra and photovoltaic characterization of chlorophyllins as sensitizers for dye-sensitized solar cells



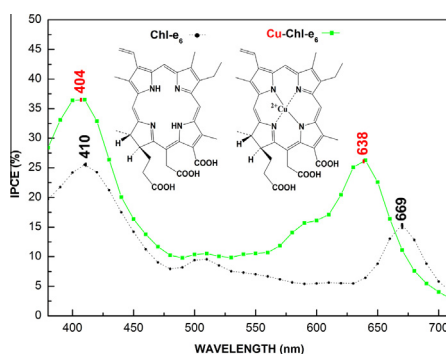
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### HIGHLIGHTS

- The influence of the solvent polarity on the dye absorption bands was analysed.
- A study of the Soret and  $Q_y$  bands of chlorophyllins was presented.
- The effect of copper on chlorophyllins' sensitizer properties was investigated.
- The dependence of solar cells performances by electrolyte composition was studied.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Dye-sensitized solar cells (DSSCs) based on Chlorine-e6 (*Chl-e6*), a *Chlorophyll a* derivative, and *Chl-e6* containing Cu, have been investigated by carrying out incident photon to current efficiency (IPCE) and current–voltage ( $I$ – $V$ ) measurements. The effect of the metallic ion and the influence of the solvent polarity on the dye aggregation and their absorption bands have been analysed by performing electronic absorption measurements. The dependence of the photoelectrochemical parameters of these DSSCs on the electrolyte by the addition of pyrimidine and/or pyrrole has been discussed in details. For the first time  $I$ – $V$  curves for a DSSC based on copper *Chl-e6* dye have been shown and compared with Zn based chlorophyllin. Furthermore, the performance of a Cu-*Chl-e6* based DSSC has been deeply improved by a progressive optimization of the  $\text{TiO}_2$  multilayer photoanode overcoming the best data reported in literature so far for this dye. It's worth to emphasize that, the analysis reported in this paper supplies very useful information which paves the way to further detailed studies turned to the employment of natural pigments as sensitizers for solar cells.

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### Introduction

Nowadays, the energetic needs matching the preservation of cleaned environment have progressively become a very important issue for the humankind. Considering that sunlight is clean,

abundant and readily available in most regions on the Earth's surface, the direct conversion of solar energy into electricity appears an attractive sustainable and environmentally friendly solution to energetic problems. Several new technologies have been developed for this purpose and, among all the devices proposed, dye-sensitized solar cells (DSSCs) represent, since the historic paper published in 1991 by Gratzel and O'Reagan [1] and up to now, the most promising systems for low cost photovoltaic energy production.

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A DSSC is a device based on the sensitization of large energy band-gap semiconductor by a dye sensitizer. Such solar cell is typically assembled by placing in tandem a photoanode (dye-sensitized semiconductor film usually based on  $\text{TiO}_2$ ), an electrolyte solution containing a redox system (iodide/iodine couple is commonly used) and a counter-electrode [2–4]. The complex working mechanism of a DSSC is mainly managed by the dye which plays a key role in light absorption and in the process of electron injection into semiconductor. In particular, to accomplish this crucial task, the sensitizer must have essential design characteristics: having an anchoring group (typically carboxylic or hydroxyl groups) to strongly bind onto the semiconductor and a remarkable solar radiation harvesting ability in a broad wavelength range from the visible to the near-IR region. Furthermore, the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the dye should have suitable energetic values. More precisely, the LUMO must be sufficiently high in energy respect to the semiconductor conduction band edge (CBE) for efficient charge injection into the  $\text{TiO}_2$ . On the other hand, the HOMO must be sufficiently low in energy respect to the redox couple of the electrolytic mediator for efficient regeneration of the oxidized dye. Finally, electron transfer from the dye to the  $\text{TiO}_2$  must also be rapid in comparison with the sensitizer decay to its ground state and the sensitizer ground and excited states must be stable [5]. Considerable efforts have been directed towards the research of the most performing dye and, over the years, the hypothesis of employing Chlorophylls to sensitize dye-sensitized solar cells has been put forward. This idea has been supported by the ability of these photosynthetic materials to convert the light into electricity and inspired by the DSSC mechanism that, for some aspects, reminds the natural photosynthesis involving light-energy absorption and charge separation [6].

Chlorophylls, which drive photosynthesis in green plants, are metal-complexes, with high symmetry, consisting of a tetrapyrrolic macrocycle coordinated to a central magnesium ion [7].

The porphyrin macrocycle is the core of chlorophyll structures and the nature of the frontier orbital in porphyrin macrocycles has been an active area of research for computational and spectroscopic investigations. Ab initio methods (restricted Hartree Fock, local density functional theory) have shown that both free base and metal (Mg(II), Cu(II), Zn(II), Ni(II)) containing porphyrins generally possess two  $a_{1u}$  and  $a_{2u}$  orbitals as the HOMO and HOMO–1 [8]. The electron density in  $a_{1u}$  type orbital is essentially localized on the C $\alpha$  and C $\beta$  atoms of the pyrrole rings, while in the  $a_{2u}$  orbital is mainly found on the pyrrole nitrogens and on the meso carbons [9].

As for the highest occupied orbitals, the lowest lying unoccupied orbitals are also similar in metal free and metal containing porphyrins: there are two nearly degenerate  $e_g(\pi^*)$  orbitals essentially centred on the porphyrin macrocycle. The persistence of  $a_{1u}(\pi)$  and  $a_{2u}(\pi)$  orbitals in diverse metal porphyrins can account for the facile formation of a  $\pi$  radical cation that plays an important role in the biochemical function of porphyrins. For example, the  $\pi$  radical cation formation is central in the photo-oxidation of chlorophyll which is essentially a Mg containing porphyrin. The nature of the frontier orbitals accounts also for the similar features in the absorption spectra of porphyrin derivatives. These show two characteristic  $\pi$ – $\pi^*$  absorption regions, the weaker  $Q_y$  band in the visible range (550–700 nm) and the intense Soret band in the near UV region (400–450 nm) [9]. Currently there are some synthetic sensitizers based on tetrapyrrolic macrocycle such as phorphyrins [10] and phthalocianines [11] which exhibit high efficiency as sensitizers but their preparation needs complicated, tedious, expensive and toxic purifications. Differently, Chlorophylls and their derivatives are environmentally friendly and cheap materials and could be prepared in the respect of the environment. Among chlorophylls, *Chlorophyll a* (*Chl a*) represents the most abundant and widespread natural compound. The first study on *Chl a* and its derivatives as

sensitizers for  $\text{TiO}_2$  nanocrystalline in DSSCs was performed in 1993 [12]. In this study the greater sensitizer ability of *Chl a* derivatives respect to the pure untreated *chlorophyll a* was evidenced. This result can be explained considering the low attitude of this natural pigment to be efficiently absorbed on  $\text{TiO}_2$  layer when dissolved in some solvent (ethanol, acetone, pyridine, etc.) due to the presence a phytyl ester group which, conversely, is eliminated in its derivatives. Furthermore, following studies have evidenced that an appropriate substitution of the functional groups bonded to the tetrapyrrolic macrocycle [13–16,7,17] or of the hosted central metal [18,19,7] represents a useful procedure to tailor the photochemical and photophysical properties of *chlorophyll a* derivatives (commonly grouped under the name of *chlorophyllins a*, such as phorphyrins, pheophorbides and chlorins).

The majority of scientific studies into the application of *chlorophyllins a* as sensitizer in DSSCs have focused on *Chlorin e6* (*Chl-e6*) with and without a central metal [12,20–23], because this dye can be easily synthesized from its precursor molecule even under mild reaction conditions.

The macrocycle of the magnesium *Chl-e6* is based on the core structure of natural *chlorophyll a* obtained by the alkaline hydrolysis of this pigment. During this process, the phytyl ester bond of *Chl a* is saponified and the cyclopentanone ring is opened with the formation of two additional carboxyl groups. Pure *Chl-e6* [23] and *Chl-e6* trisodium salt [20] sensitized solar cells have shown a photoenergy conversion efficiency of 0.4% and 0.73%. Recently, this efficiency was increased to 0.9% by applying a scattering nanoparticles coating onto the  $\text{TiO}_2$  layer [17].

A further analysis has revealed improved values of the current density and of the open circuit voltage for a solar cell sensitized by *Chl-e6* coordinated to zinc ion [24]. Moreover, in 1993, Kay and Grätzel [12] evidenced that copper *Chl-e6* is an excellent photosensitizer for  $\text{TiO}_2$  with a 70% of the incident photons converted into electrons but no photocurrent–photovoltage study was performed on this DSSC.

With the aim to provide a further piece of information about metal substituted *Chl-e6* based DSSC, in this paper electronic absorption and photocurrent action spectra, together with photocurrent–photovoltage curves for *Chl-e6* and copper *Chl-e6* solar cells are presented and compared with the existent literature. The influence of the solvent polarity on the dye absorption bands is analysed. Finally, the dependence of the DSSC performance on the electrolyte pH, on the dye central metal, on the employment of a white or mirror reflector behind the cathode, on the  $\text{TiO}_2$  film thickness and on the presence of a scattering coating on this semiconductor layer are discussed in detail.

## Experimental section

### Materials

All the solvents and the other chemicals employed for the experiments were reagent or spectrophotometric grade and were used as received without any further purification. The conductive glassy plate (FTO-glass, Fluorine-doped  $\text{SnO}_2$ , sheet resistance 7  $\text{ohm/cm}^2$ ), and the Surlyn foils (thickness: 25  $\mu\text{m}$ ) were purchased by Solaronix SA, while Ti-nanoxide (T/SP) was purchased by Dyesol. The investigated chlorophyllins, chlorin-e<sub>6</sub> (B10) and Copper chlorin-e<sub>6</sub> (A10) (see Fig. 1), were obtained by *chlorophyll a* according to a well known procedure [25].

### Preparation of $\text{TiO}_2$ anodes

The FTO-glass, used for the preparation of transparent electrodes, was first cleaned in a detergent and then washed with

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