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Review

β-Substituted Zn^{II} porphyrins as dyes for DSSC: A possible approach to photovoltaic windows

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A B S T R A C T

The development of building integrated photovoltaic (BIPV) technology and its implementation in construction of the building envelop provide aesthetical, economical and technical solutions toward the zero-energy building. In this perspective dye-sensitized solar cells (DSSCs), which can be obtained in transparent form and with tunable different colors, offer not only an alternative to the traditional silicon solar cells to be applied in particular to decorative effects on windows and glass integrated façades, but also to indoor structures (and furnishings) in order to recapture the energy spent for the inner lighting, thanks to their peculiar ability of operating in diffuse light condition.

In this context, porphyrin-based molecules have an immense potential as light harvesting component of dye-sensitized nanocrystalline TiO_2 solar cells, reaching now efficiencies up to about 13%. However the multistep synthesis of the best performing porphyrin dyes, showing a *meso* substitution pattern, is characterized by very low overall yields compromising their possible applicative development for instance in large photovoltaic (PV) glass modules in competition with the actual commercial PV glass modules based on $CuInGaSe_2$ or CdTe thin voltaic films.

In this review the renewed interest in the role of the β-substituted Zn^{II} porphyrins for PV application, less studied than the *meso* substituted ones, is highlighted. Indeed they can rely on a more accessible synthetic procedure since their tetraaryl porphyrinic core can be easily obtained by a one pot reaction between pyrrole and the appropriate aryl aldehyde. Moreover, their remarkable light harvesting properties in the visible range as well as their peculiar steric hindrance, which strongly opposes to the charge recombination process at the photoanode/dye/electrolyte interface, make this kind of cost-effective porphyrinic dyes more promising for application in new PV glass modules based on DSSC technology, to be applied BIPV.

Contents

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1. Introduction

The first installation of photovoltaic (PV) modules as glass elements integrated into a wall façade with isolating glass was realized in 1991. Since then the building-integrated photovoltaics (BIPVs) developed quite rapidly. Today a standard-size module for PV façades or roof installations reaches 1 MW output [1].

Commercial BIPV glass modules are constituted by a thin layer of mono or multi solar cells, based on the traditional crystalline or amorphous silicon semiconductor embedded into resin foils between two glass planes. Although the actual commercial solutions already give some interesting advantages such as daylighting, shading, noise reduction and, most relevant, electricity production, there is in the modern architecture an increasing demand for alternative PV glass modules, which can introduce new decorative and specific lighting solutions [2].

These solutions could offer a high degree of freedom for the design (not only geometric) and aesthetics of a building integrated module. With this objective, since the last 10–15 years dye-sensitized solar cell (DSSC) technology has been considered as a potential basis of new building integrated PV modules. In fact, starting from the pioneering work by O'Regan and Grätzel in 1991 [3], DSSCs have emerged as an alternative to conventional silicon-based solar cells, being low cost photovoltaic devices with interesting power conversion efficiency. Since DSSCs can be obtained in transparent form and with tunable different colors, they can be potentially interesting for their application in PV glass integrated façades or "smart" windows [4–10].

Moreover DSSCs are characterized by the peculiar ability of operating also in diffuse light condition [11]. This feature can be exploited for the internal structures (e.g., transparent walls [12]), doors or furnishings in order to obtain a recovery of the energy spent for the internal lighting.

Such a versatile applicability to outdoor/indoor environmental makes DSSC a potential solution to satisfy the technological requirement for the integration of renewable energy resources in construction of the building envelop and toward the definition of the zero-energy-building standards [13,14], as required by several countries by 2020, in order to contribute in the limiting of the greenhouse gas emission [15].

The standard design of a DSSC comprises a dye sensitized photoanode (TiO_2) and a platinum counter electrode with a liquid electrolyte redox mediator (for example based on I_3^-/I^-, Co^{II}/Co^{III} or more recently on $Cu^{+/2+}$ [16]) filling the space between anode and cathode (Fig. 1).

By photoexcitation an electron is transferred to the excited state orbitals of the dye, followed by injection of the excited electron into the conduction band of the TiO_2 semiconductor, resulting in the oxidation of the dye. The injected electron diffuses through the TiO_2 photoanode toward the transparent conducting glass and reaches a platinum counter electrode through the external wiring. The oxidized dye is then reduced by means of a process involving for instance the I^- ions of the electrolytic mediator, regenerating its ground state, while the resulting I_3^- ions are reduced to I^- ions by the counter electrode, in this way completing the electrical circuit (Fig. 1).

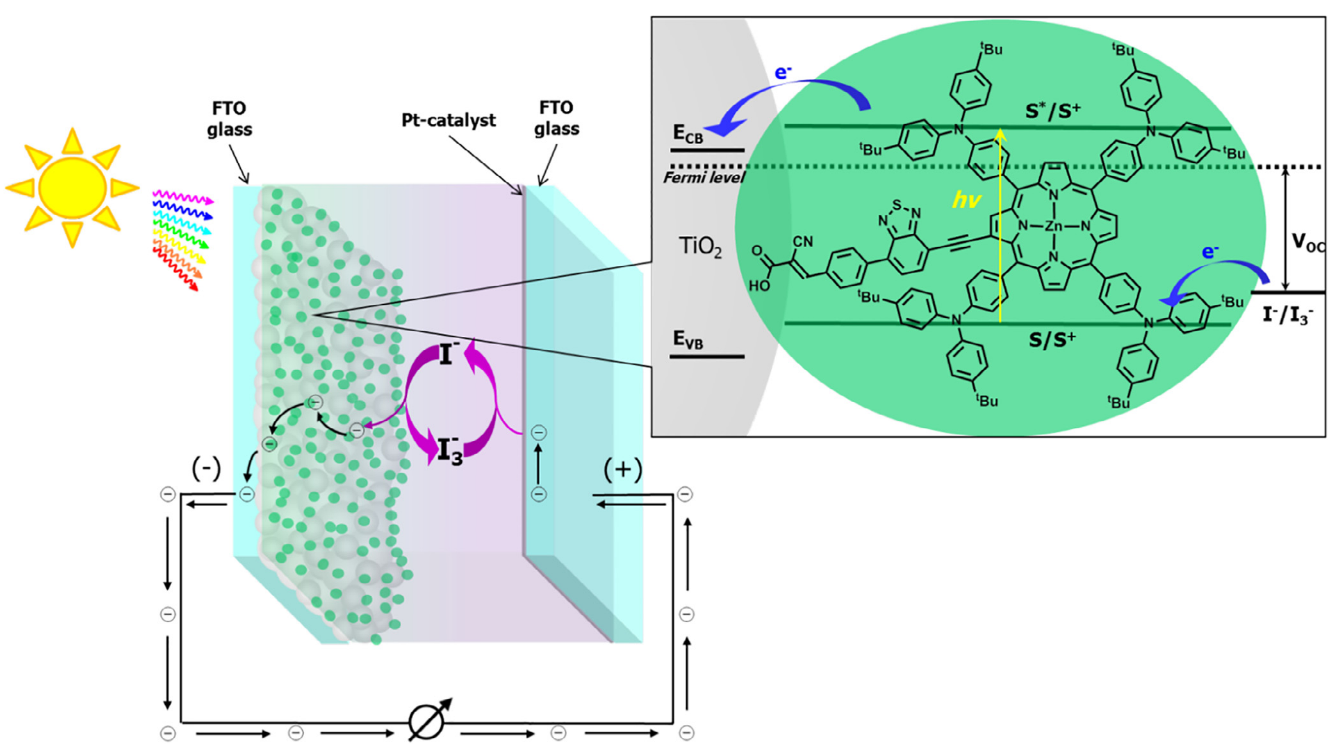

Fig. 1. Schematic diagram illustrating the working principle of a DSSC.