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(SRI -VIPRA)**

SRI-VIPRA

Project Report of 2024: SVP2419

“Pyridine-Based Donor Dye in Dye Sensitized Solar Cells”

IQAC


Sri Venkateswara College

University of Delhi


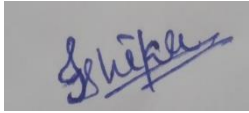

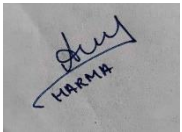
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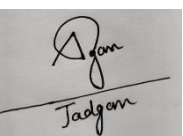
SRI-VIPRA Project 2024

Title : Pyridine-Based Donor Dye in Dye Sensitized Solar Cells

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Certificate of Originality

This is to certify that the aforementioned students from Sri Venkateswara College have Participated in the summer project **SVP-2419** titled “**Pyridine-Based Donor Dye in Dye Sensitized Solar Cells**”. The participants have carried out the research project work under my Guidance and supervision from 1st July, 2024 to 30th September 2024. The work Carried out is original and carried out in an online/offline/hybrid mode.

T. chandra sekhar

Signature of Mentor

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Abstract

This review explores the advancements in dye-sensitized solar cells (DSSCs), focusing on the role of porphyrin-based dyes as promising alternatives to conventional solar technologies. As global energy demands rise and environmental concerns escalate, the need for sustainable energy solutions is critical. In this review, we discuss a collection of three sets of porphyrin-based systems. In the first set we would improve the light harvesting ability of porphyrins by preparing arrays in which strongly absorbing boron dipyrin (BDP) chromophores are combined with porphyrins, either by covalent attachment to the periphery of the porphyrin ring or by axial coordination to a Tin(IV) porphyrin. In the second set, we use porphyrins as sensitizers in photocatalytic hydrogen production schemes with cobaloxime catalysts either in supramolecular or diffusion controlled systems. In the third set, the porphyrins are used as light harvesting dyes in dye-sensitized solar cells (DSSCs). These include porphyrins with p-conjugated groups at meso positions, “push–pull” porphyrins, porphyrins with bridges between the macrocycle and the anchoring group, and covalently linked arrays of porphyrins and other chromophores [1,2].

Introduction

In recent years, global energy consumption has gone up significantly, especially because of population growth in developing countries. Most of our energy still comes from fossil fuels like coal, oil, and natural gas, which make up about 80% of what we use. However, using these fuels causes environmental pollution. The growing energy needs, the shrinking supply of fossil fuels, and the negative environmental effects of fossil fuel-based technologies are pushing scientists to find eco-friendly alternative energy sources. One promising alternative is solar energy. It's appealing because of a technology called artificial photosynthesis. In 1991, Grätzel and his team introduced Dye Sensitized Solar Cells (DSSCs), a groundbreaking solar technology. DSSCs are popular in the field of solar energy because they are inexpensive to produce and have a high efficiency in converting sunlight into electricity. Many researchers are focusing on dye-sensitized solar cells (DSSCs) because they show good potential with power conversion efficiency (PCE) over 11% and can be easily made on flexible surfaces. Dye-sensitized solar cells (DSCs) are a cost-effective solar technology that works well in low-light conditions. These cells are useful for building-integrated solar panels and indoor devices, such as those used for the Internet of Things (IoT). Based on the recent results from the group on the use of porphyrins as light harvesting and energy storage agents in three different contexts: (i) synthesis and photophysical study of different porphyrin molecules (ii) The use of porphyrins as sensitizers in photocatalytic hydrogen production schemes (iii) porphyrin derivatives as light harvesting dyes in dye sensitized solar cells (DSSCs) [1,2,3].

Electron and energy transfer in porphyrin derivatives

Boron dipyrin (BDP), dyes are particularly attractive as “antenna” chromophores for porphyrins as they combine the following characteristics: (i) BDPs are well-known for their high extinction coefficients in the 450–550 nm region (ii) high fluorescence quantum yields and long-lived excited states and (iii) excellent photostability, and stability in many solvents [3].

Porphyrin arrays linked via a cyanuric chloride bridge

P1 and P2 were further functionalized with an electron accepting fulleropyrrolidine through an amino substituted aliphatic chain to give electron donor/acceptor conjugate P3 and P4. Triads P3 and P4 show a triangular arrangement of three different photo- and redox- active groups around the central s-triazine linker thereby permitting direct interaction of each chromophore with the other two. The excitation of P1 and P2 into their BDP-based singlet p-p'/excited states is followed by energy transfer to the lowest-lying porphyrin based singlet excited states with rate constants of $k_{P1} = 2.9 \times 10^{10} \text{ s}^{-1}$ and $k_{P2} = 2.2 \times 10^{10} \text{ s}^{-1}$. The transient absorption studies of triads P3 and P4, selective BDP excitation at 490 nm results in the immediate formation of the BDP singlet excited state which decays by energy transfer to the porphyrin singlet excited state with time constants of 32 and 26 ps respectively. [3,4]

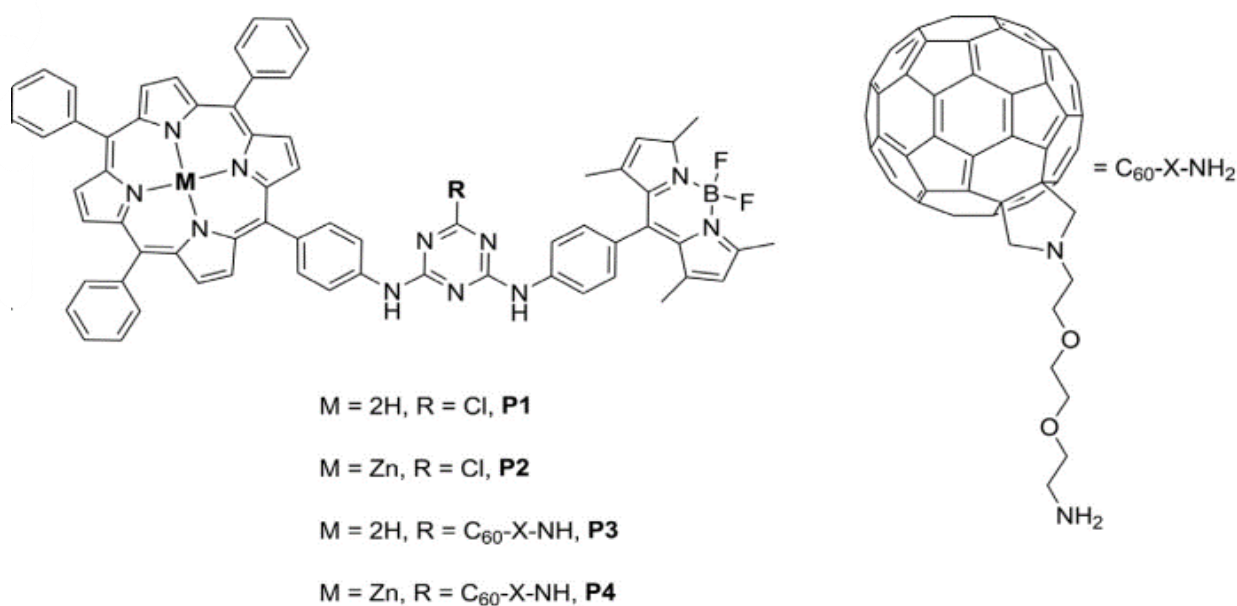


Fig. 1 Peripherally substituted porphyrin arrays linked through a cyanuric chloride bridge.

Porphyrin arrays linked by an amino group

Triads P5 and P6 were prepared, where two H2P or BDP units were linked to the meso positions of a central ZnP via amino groups. Most notable in the UV-Vis spectra of P5 and P6 is their wide range absorption over most of the visible region. When P5 is excited at either 517 nm (mostly peripheral H2P chromophores) or 467 nm (mostly central ZnP chromophore) an emission spectrum resembling that of a free base porphyrin is obtained with maxima at 661 and 719 nm, while the excitation spectrum of P5 shows absorption features from both the central and peripheral porphyrins when monitored at 661 nm. In the case of P6, both steady-state and time resolved emission spectra clearly show that excitation of the BDP units into their first singlet excited state at ca. 490 nm is followed by rapid energy transfer to the corresponding ZnP singlet excited state. [4,5]

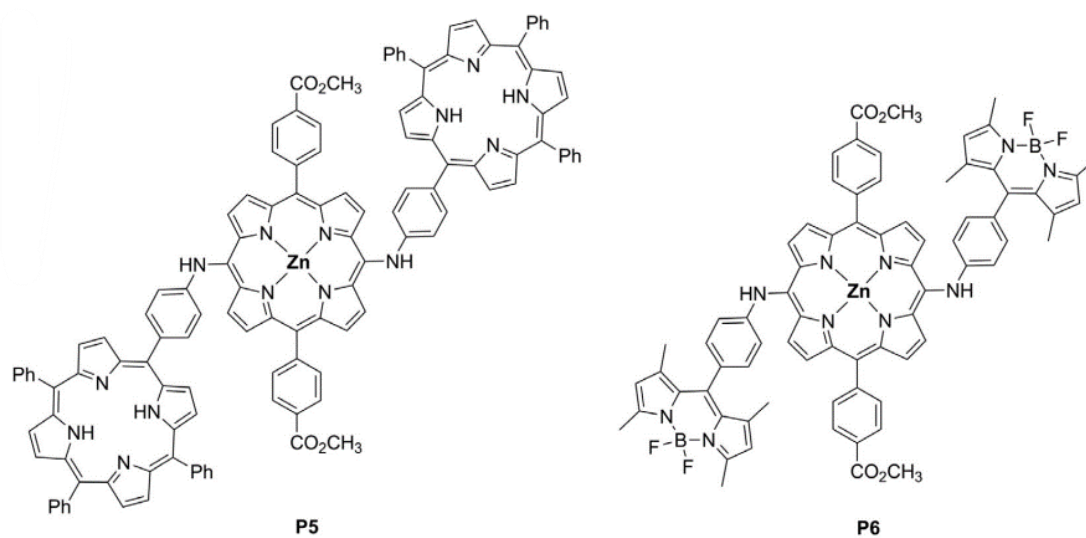


Fig. 2 Peripherally substituted porphyrin arrays linked through an amino group.

Axially linked porphyrin arrays

Initial study of P7 and P8 by cyclic voltammetry and UV-Vis absorption spectroscopy once again reveals weak ground state interchromophoric interactions as well-resolved signals. The CS state recombines back to the singlet excited state with a lifetime of 450 ps. The absence of an oxidizable phenoletate moiety in P8 reflects its different dynamic behaviour [5].

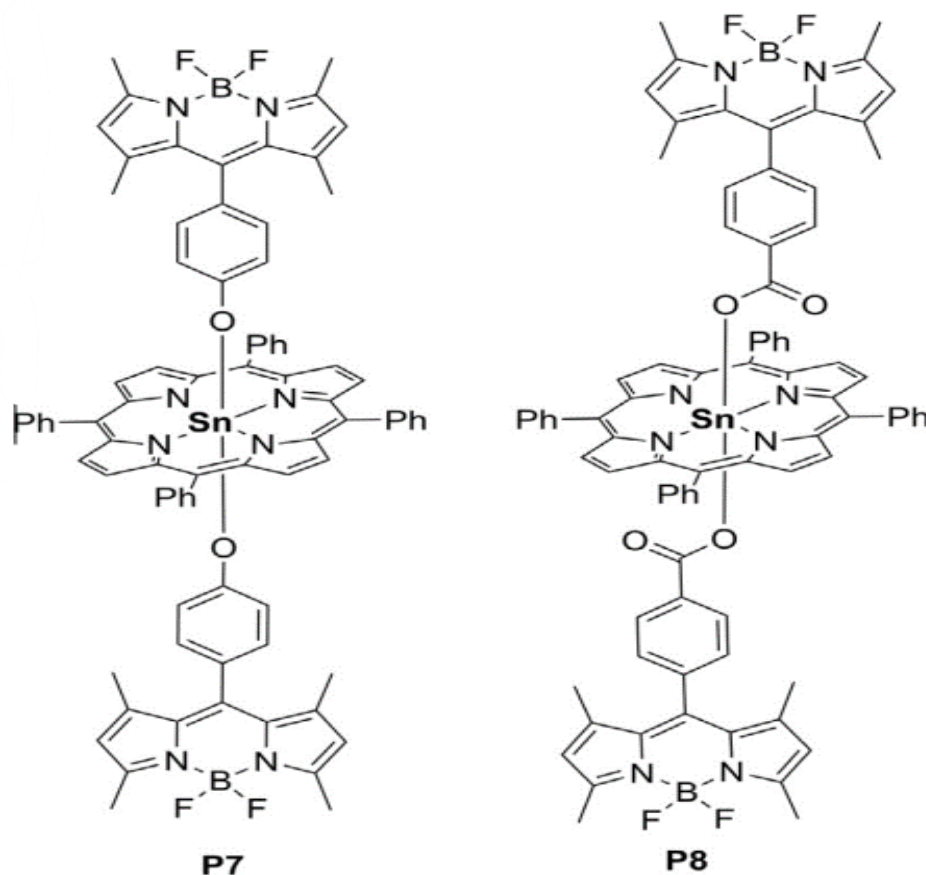


Fig. 3 Axially linked BDP-porphyrin arrays

Study of porphyrin-cobaloxime and corrole-cobaloxime hybrids

Transient absorption spectra show that the singlet excited state features of the porphyrins and corrole in P9–11, formed after photoexcitation, decay with ultrafast kinetics (lifetimes of 380, 81 and 680 ps for P9, P10 and P11 respectively) without the formation of a photoproduct.

In experiments to access the photocatalytic activity of P9–11, the conjugates were irradiated with visible light in deoxygenated tetrahydrofuran/H₂O 4:1 in the presence of triethylamine and only the ZnP derivative was found to be only modestly active producing about 3 turnovers of H₂ after 24 h.

The excitation of the porphyrin Q bands (at 572 nm using a 10 nm FWHM bandpass filter) also leads to H₂ production thereby unambiguously confirming that P12 acts as a photosensitizer, the P12 singlet excited state does not participate in the photocatalytic process since its lifetime is similar to that reported for P12 alone in aqueous solution. Results show that H₂ is produced following the generally accepted mechanism involving a catalytically active CoI species produced by sequential reduction of the initial CoIII complex mediated by the first triplet excited state of P12. [5,6]

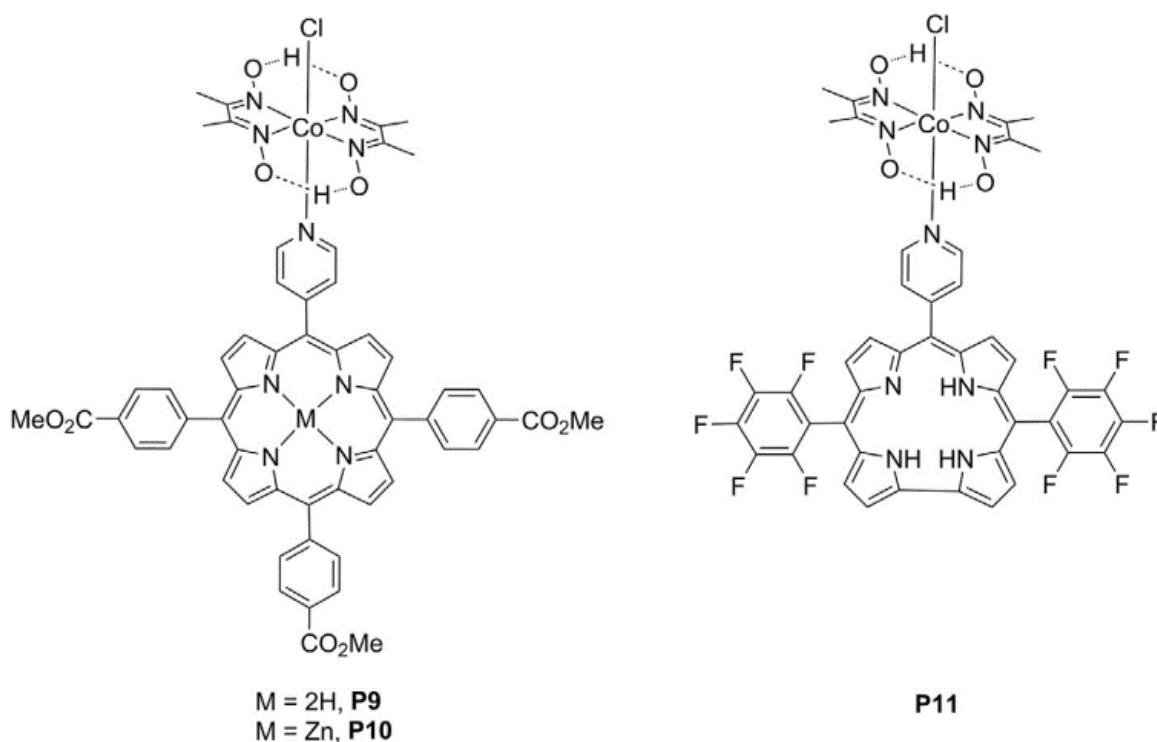


Fig. 4 Supramolecular photosensitizer-catalyst systems

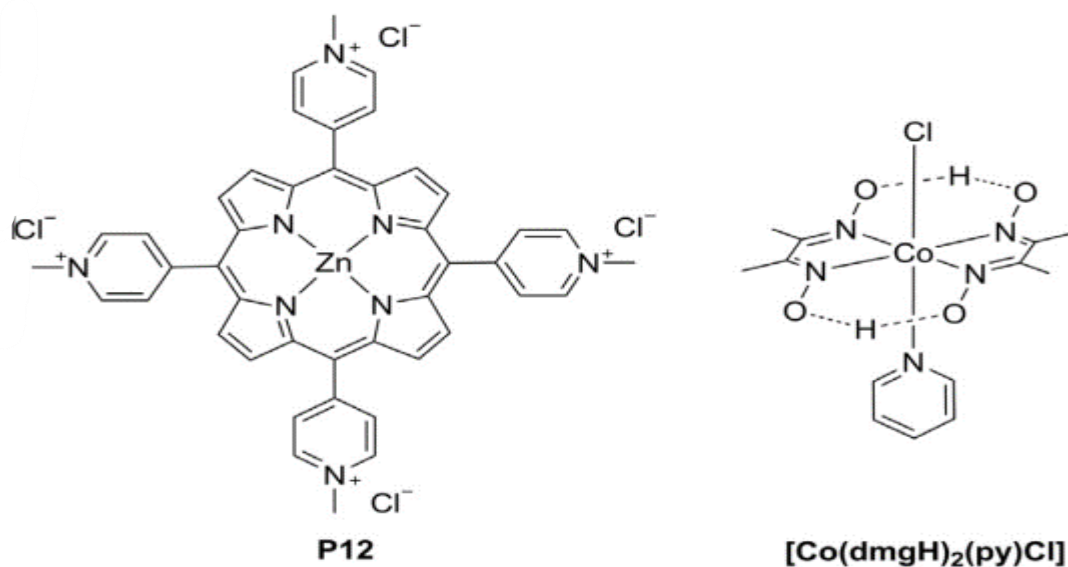


Fig. 5 Photosensitizer (P12) and catalyst (cobaloxime) of the diffusion controlled photocatalytic H₂ production system.

Porphyrin derivatives as light harvesting dyes in DSSCs

A typical device consists of three components: (a) a photoanode composed of a mesoporous, nanocrystalline semiconductor film (such as TiO₂) on a transparent conductive oxide (TCO) glass substrate, on which a monolayer of a sensitizer has been attached; (b) a cathode, which is a platinum-coated TCO glass; (c) a molten electrolyte containing a redox couple that fills the space between the two electrodes.

Porphyrins, owing to their excellent light harvesting potential in mimicking photosynthesis, stimulated significant interest as sensitizers for DSSCs. By rational molecular design and synthesis, they can be appropriately functionalized at meso or b positions, at the periphery, or the central metal of the macrocycle, allowing fine control of their photophysical and electrochemical properties.

More recently, a similar porphyrin that maximizes electrolyte compatibility and exhibits improved light harvesting efficiency resulted in an overall efficiency of 13% [7,8].

Porphyrins with π -conjugated groups at meso positions

In general, porphyrins, due to their weak light harvesting ability in the green and red regions of solar spectrum, result in poor photovoltaic efficiencies.

Absorption broadening has a profound effect on the HOMO–LUMO gap of P13, found to be 1.90 eV, as indicated by electrochemistry data. The IPCE spectrum of P13 displayed very broad Soret and Q band absorptions with maximum values of 65 and 60%, respectively. The use of deoxycholic acid (DCA) as co-adsorbent in a P13 sensitized solar cell resulted in the enhancement of its photovoltaic parameters and its overall efficiency to 4.22%, despite the concurrent reduction of the amount of dye adsorbed onto the TiO₂ surface. [8,9]

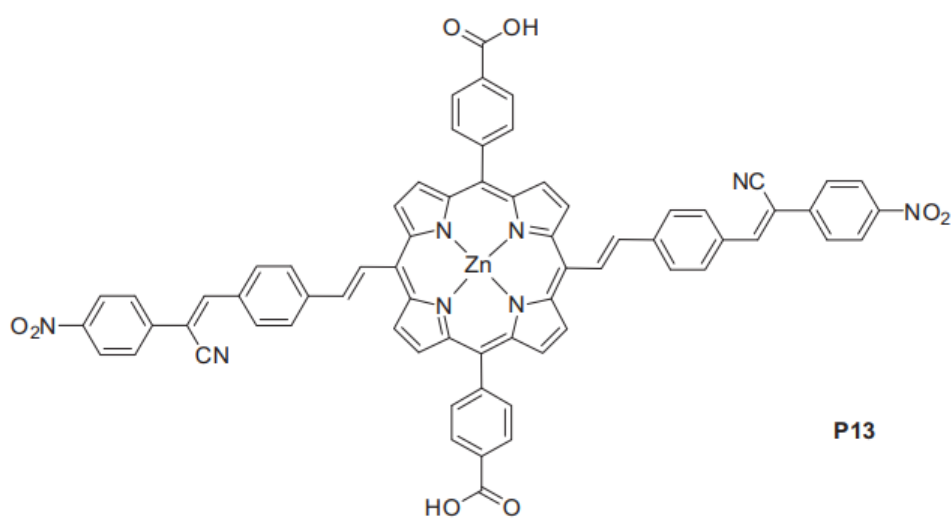


Fig.6 Porphyrin P13 with π conjugated groups at meso positions

“Push–pull” porphyrin

This type of porphyrins are based on a donor- π -acceptor (D- π -A) architecture, in which p represents the π conjugated porphyrin macrocycle (the light harvesting center), D is an electron donating group, and A is the electron accepting group (usually, the highly polar carboxylic acid anchoring group).

We synthesized two “push–pull” porphyrin derivatives, namely P14 and P15.

Photovoltaic measurements of the DSSCs sensitized by P14 and P15 revealed enhanced photovoltaic parameters and higher PCE value for the latter solar cell 3.80% and 4.90%.

This was attributed to a higher amount of P15 adsorbed onto the TiO₂ surface, arising from the stronger affinity of P15 for TiO₂. [9]

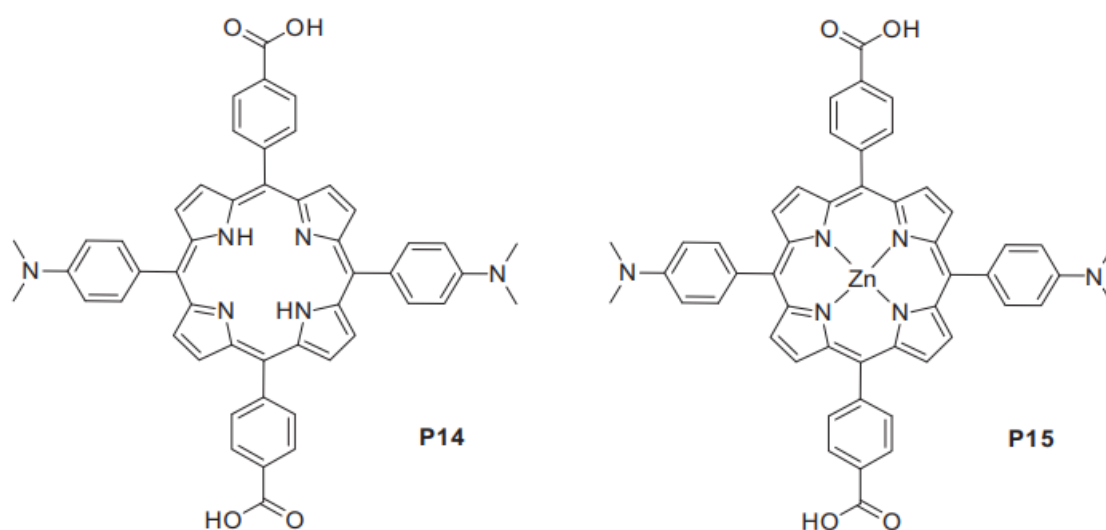


Fig.7 “Push–pull” porphyrins P14 and P15

Pizzotti and their team compared two types of zinc porphyrins used in solar cells: one type with a single special group added (mono-substituted) and another type with two special groups added in a "push-pull" arrangement. Even though the push-pull type has a smaller energy gap between its highest occupied and lowest unoccupied molecular orbitals (HOMO-LUMO), which should theoretically make it better at transferring charge, the single-group-added (mono-substituted) porphyrins actually performed just as well, or even better, in the dye sensitized solar cells. [10]

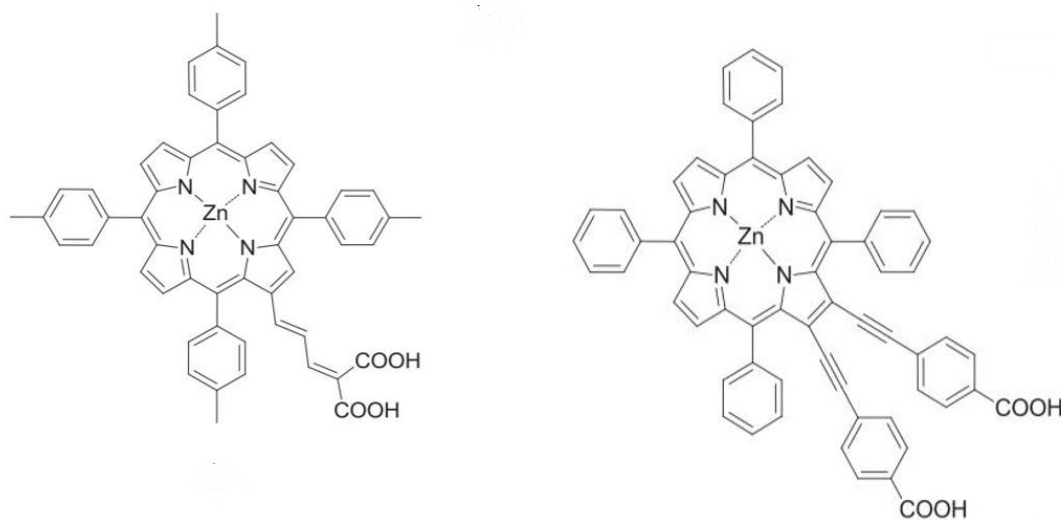


Fig.8 Molecular structure of Zn Porphyrin Dye

Porphyrins with bridges between the macrocycle and the anchoring group

We have synthesized two porphyrin derivatives of the D-p-B-A type, namely the compounds P16 and P17 (Fig.8), in which B represents an ethynyl bridge attached to two opposite meso positions of the porphyrin macrocycle, terminated by a carboxylic acid anchoring group (A) and a donor group (D).

Their corresponding solar cells were found to exhibit poor photovoltaic parameters and overall efficiencies of 1.58% and 2.84%, respectively.

The slightly better performance of P17 might be ascribed to the stronger amine electron donating group opposite to the carboxylic acid anchoring group. [11,12]

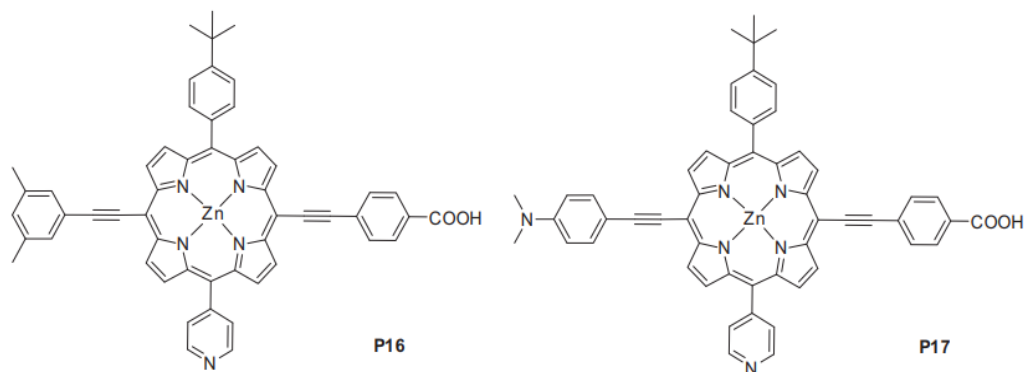


Fig.9 Porphyrins P16 and P17 with ethynyl bridges between the macrocycle and the anchoring groups.

Covalently linked arrays of porphyrins and other chromophores

Porphyrin dyads P18–19 (Fig.10), in which two porphyrin units (either in their zinc-metallated or free-base forms) are covalently linked through peripheral aryl-amino groups by the π -conjugated unit of s-triazine. The compounds are functionalized by terminal carboxylic acid groups, either on the central triazine unit or on a peripheral aryl group. The P18 and P19 sensitized solar cells were found to exhibit PCE values of 3.61% and 4.46%, respectively.

The superior performance of P19 can be explained on the basis of its unsymmetrical structure and the presence of a free-base and a zinc-metallated unit in P19 might cause a polarizing and cooperating effect that directs the electron transfer to the TiO₂ CB, and leads to more efficient electron injection, while in the symmetrical P18 there is no directionality in the electron transfer process. [12]

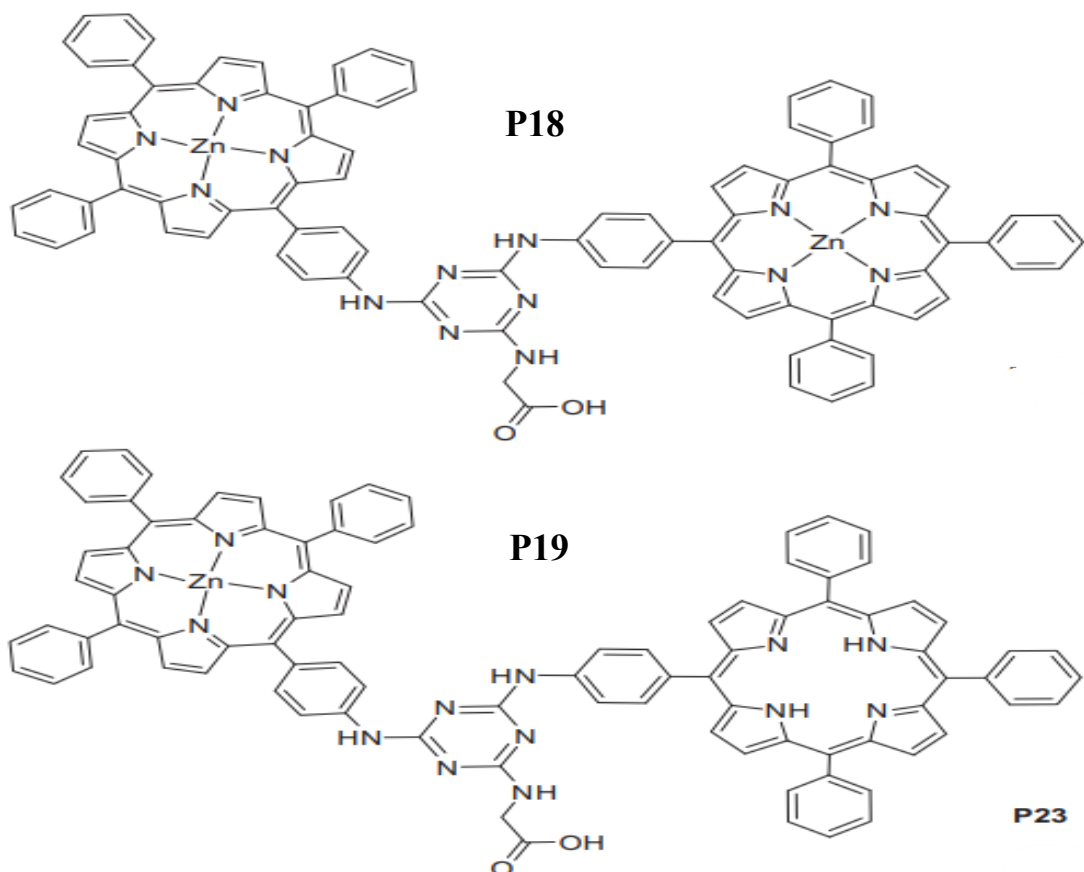


Fig.10 Porphyrin dyads P18–19 covalently linked by s-triazine

Conclusion

Dye-sensitized solar cells (DSSCs) present a promising and cost-effective alternative to traditional solar technologies, particularly in applications requiring flexibility and performance under low-light conditions. Their inexpensive and abundant materials, along with our ability to fabricate them as thin and light-weight flexible solar panels makes them well-suited for producing low-cost indoor solar panels. Despite the significant progress made since their introduction, the efficiency and commercial viability of DSSCs are still hampered by issues such as limited light absorption and dye aggregation. Recent advancements, particularly the development of porphyrin-based dyes with D- π -A structures, have shown considerable potential in addressing these challenges, enhancing light absorption porphyrin-based excited states are efficiently sensitized by the presence of strongly absorbing boron dipyrin (BDP) chromophores both as substituents at the periphery of the porphyrin ring and as axial ligands through rapid BDP to porphyrin excitation energy transfer. We have confirmed that diffusion controlled photocatalytic systems show far greater activity than supramolecular ones because the latter suffer from rapid back electron transfer which prevents the, essential for H₂ production, accumulation of a reduced catalytic species. In an effort to obtain suitable porphyrin-based sensitizers for DSSCs, a variety of functionalized porphyrins with carboxylic acid anchoring groups were designed and synthesized. Porphyrins with p-conjugated groups at meso positions, “push-pull” porphyrins, porphyrins with bridges between the macrocycle and the anchoring group, and covalently linked arrays of porphyrins and other chromophores were used for the fabrication of DSSCs.

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