

PHOTOELECTROCHEMISTRY OF BIOMIMETIC MOLECULES. SPECTRAL SENSITIZATION OF WIDE BAND GAP OXIDE SEMICONDUCTOR ELECTRODES BY SUPRAMOLECULAR ORGANIC DYES

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*Received April 12, 2003. Accepted in Final Form June 9, 2003
Dedicated to Professor Dr. A.J. Arvia on occasion of his 75th Anniversary*

Abstract

The generation of photoelectrical effects through the spectral sensitization of wide band gap semiconductor electrode by the excitation of a series of novel synthetic organic molecules is reviewed. Natural Photosynthetierelated supramolecular systems where designed and constructed in order to obtain “antenna” and intramolecular charge transfer process. The dyes were adsorbed to saturation on nanocrystalline SnO₂ thin films or deposited as Langmuir-Blodgett films, and employed as working electrodes in a photoelectrochemical cell. The close match between the photocurrent action spectrum and the absorption spectrum showed that the photoensitization mechanism is operative in extending the photocurrent response to the visible region, and demonstrated that the excitation of organic dyes results in the generation of photoelectric effects, with high yield and light harvesting capacity.

Resumen

En este trabajo se reseña la generación de efectos fotoeléctricos, a través del proceso de sensibilización espectral de electrodos semiconductores, por medio de una serie de moléculas orgánicas sintéticas. Se diseñaron y construyeron sistemas orgánicos supramoleculares en los cuales un efecto “antena” y procesos de transferencia de carga intramolecular fotoinducidos pueden ocurrir como paso previo a la inyección heterogénea de cargas. Los colorantes se adsorbieron sobre películas finas de SnO₂ nanoestructurado y como depósitos de Langmuir-Blodgett para emplearlos como electrodos de trabajo en celdas fotoelectroquímicas. La total concordancia entre los espectros de absorción y de fotocorriente demuestra que el mecanismo de fotosensibilización efectivamente ocurre, extendiendo la generación de efectos fotoeléctricos a la región visible del espectro, y demostrando que la excitación de los colorantes orgánicos resulta en la generación de efectos fotoeléctricos, con alto rendimiento.

Introduction

The search for cost-effective solar cells has been a field extremely active of investigations since the middle of the last century. In conventional solid-state

photovoltaic devices electron-hole pairs are created by semiconductor light absorption, and charge separation is obtained under the influence of a built-in electric field. A different approach is the spectral sensitization of wide band gap semiconductors, where the energy difference between the conduction band edge of a n-type semiconductor film and the oxidation potential of the excited sensitizer (E_{ox}^*) present as an adsorbate provides a driving force for excited state charge injection and the generation of photoelectric effects [1,2] (Figure 1). Over the basis of modern organic chemistry a remarkable progress in the energy conversion yield can be reached, mainly due to the nearly unlimited variability of the organic materials, which can be designed with special structural and electronic properties. Such properties must be adequate in order to have efficient light absorption in the solar spectra wavelength region, redox reversibility, and long-term photochemical stability [1,2].

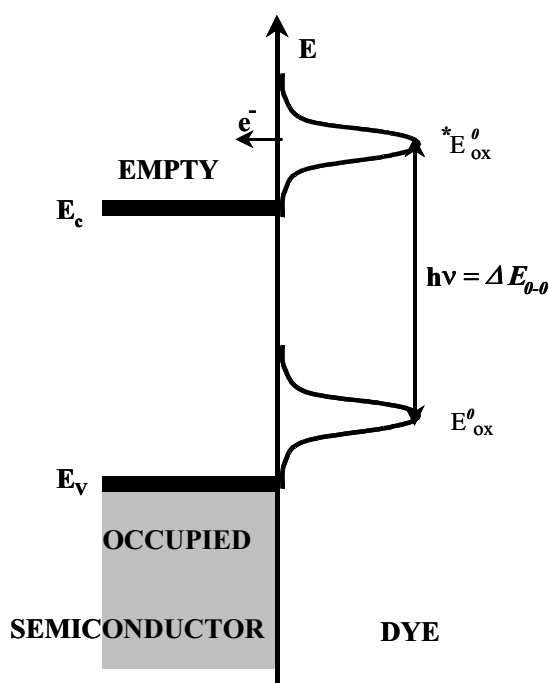


Figure 1: Energy level diagram for the spectral sensitization of ITO/SnO₂/dye electrode.

Unfortunately, however, only the first monolayer of the adsorbed dye produces a significant photoeffect, and the light-harvesting efficiency of a single monolayer is very low. Nevertheless, in a porous film of nanometer-sized semiconductor particles, the effective surface area can be greatly enhanced, producing substantial light absorption even with only a monolayer of dye on each particle [3-12]. Using this advantage, the spectral sensitization of wide band gap metal oxide semiconductors with organic dyes is of great interest in the search of efficient energy conversion devices [13,14]. A considerable number of organic structures has been designed, synthesized and studied with this purpose, and, like us, many researchers were inspired in this field by the natural photosynthetic apparatus [15-24].

Photoinitiated transmembrane electron transfer to yield long-lived charge-separated states is the basic energy conversion process of natural photosynthesis. In the protein environment of photosynthetic reaction centers a series of short-range, fast, and efficient electron-transfer steps are carried out, which move electrons and holes to opposite sides of the membrane [25]. It has been described that photoinduced electron transfer involving cyclic tetrapyrrole molecules (the special pair of bacteriochlorophylls) is the primary step in the mechanism of photosynthetic bacteria, but most of the absorbed light is supplied to the reaction center of the photosynthetic apparatus by singlet-singlet energy transfer from antenna systems, where carotenoids play a very important role. They strongly absorb light in the 400-550 nm region, and their singlet states can transfer excitation energy through singlet-singlet mechanism to chlorophyll molecules [26].

Given the crucial role of photosynthesis in natural solar energy conversion, it is not surprising that great effort has been made to mimic this solar energy harvesting device [27,28]. Synthetic multicomponent molecules that mimic both energy and electron transfer have been reported [29] and recently even artificial photosynthetic membrane have been designed and constructed [30,31]. In these membranes a vectorial photoinduced electron transfer is produced in a carotene-porphyrin-naphthoquinone (C-P-Q) molecular triad, which is able to generate proton [30] or calcium [31] pumps. The photogenerated $C^{\bullet+}$ -P-Q $^{\bullet-}$ state is coupled to proton or calcium translocation by specific quinones that alternate between reduced and oxidized forms.

Another approach to mimic the photosynthetic energy conversion system in nature is the use of the energy stored in these synthetic molecular arrays as photoinduced intramolecular charge separation state for to generate an electric work through an external circuit in a suitable photoelectrochemical cell [1-3]. As it has been pointed out [6] there are several analogies between the natural photosynthesis and the dye-sensitized nanocrystalline semiconductor electrodes using electron donor-acceptor molecular assemblies [32]. Nature uses a similar way of absorption enhancement by stacking the chlorophyll-containing thylakoid membranes of the chloroplast to form the grana structure [15].

In our studies we have focused our interest in the study of heterogeneous photoinduced charge transfer process involving organic synthetic molecules related to the natural photosynthesis. These molecules are specially functionalized carotenoids [33-35] porphyrin-porphyrin molecular dyads [36-38] and covalent linked porphyrin-C₆₀ fullerene supramolecular systems [39-41] (Figure 2). The formation of organic molecular assemblies (self adsorption or Langmuir-Blodgett films) over semiconductor electrodes allowed us the analysis of the generation of photoelectric effects produced by excitation of the different dyes. Our results showed that efficient light harvesting and charge transfer yield can be reached using molecular arrays inspired in the natural photosynthetic apparatus.

Experimental

Preparation of SnO₂ Nanocrystalline films Photoelectrodes.

Optically transparent electrodes were cut from indium tin oxide (ITO) coated glass plates. ITO/SnO₂ electrodes were prepared by spin coating using a 1.5% SnO₂

colloidal suspension (15 nm particular diameter) in water containing a surfactant (Triton X-100). The resulting films (thickness 0.2 μm), which are transparent in the visible region (absorbance at 500 nm around 0.02), have strong absorption in the UV with an onset at around 355 nm (this onset absorption corresponds to a bulk band gap of 3.5 eV) [22, 35-41].

The ITO/SnO₂ electrodes were modified with the dyes showed in Figure 2 by soaking overnight ITO/SnO₂ films in a solution of the corresponding dye.

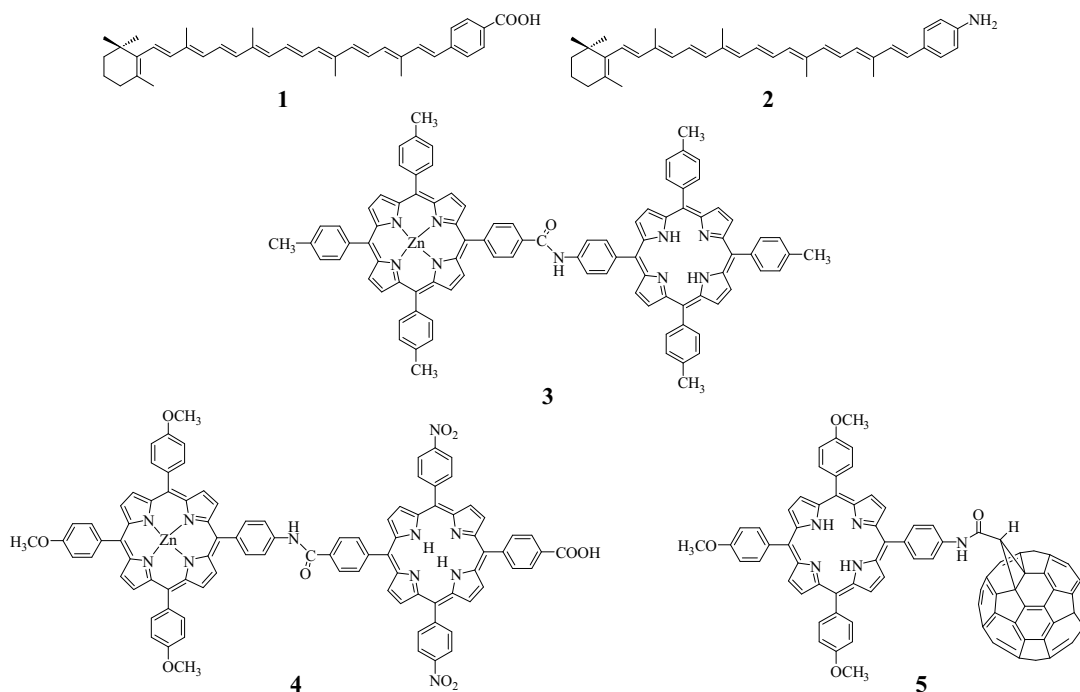


Figure 2: Structures of the sensitizing dyes.

Langmuir-Blodgett (LB) Film Preparation.

Monolayers were prepared on a Model 610 Nima Langmuir-Blodgett trough. The subphase was ultrapure water with phosphate buffer (pH = 5.2). The substrates for monolayer depositions were transparent ITO electrodes. Only films having transfer ratios of 1.0 ± 0.1 were used in the experiments [33-35].

Photoelectrochemical Measurements.

Photoelectrochemical experiments were conducted in degassed aqueous solutions (0.01 M) of hydroquinone, with phosphate buffer (pH = 5.2). The measurements were carried out in a 10 mm quartz photoelectrochemical cell equipped with Ag/AgCl as reference electrode, and Pt foil as the auxiliary electrode. Action spectra for photoelectrodes were obtained by sending the output of a 150 W high-pressure Xe lamp through a high intensity grating monochromator and recording the resulting steady-state photocurrent. All the photoelectrochemical measurements were done in front face configuration and the incident light intensities at different wavelengths were measured with a Coherent Laser-Mate Q radiometer [22, 35-41].

Absorption and emission spectroscopy.

Absorption spectra were recorded on a Shimadzu UV-2401PC spectrophotometer. Fluorescence spectra of dyes were recorded on a Spex FluoroMax fluorimeter, provided of solid sample holder.

Electrochemistry.

For cyclic voltammetry (CV) a potentiostat-galvanostat EG & G Princeton Applied Research PAR-273 and a conventional three compartment Pyrex cell was used.

Synthesis of Dyes.

The structures of the molecules are shown in Figure 2. They were prepared using already described methods [33-41]. Amphiphatic carotenoids **1** and **2** were prepared by Wittig reaction between of 8'-apo- β -caroten-8'-al and the corresponding phosphonium salt derivative. This reaction produce the ester and amido carotenoids, which were hydrolyzed in basic medium to obtain the carotenoids **1** and **2**, respectively [33-35]. Asymmetric substituted porphyrins were synthesized from the condensation of *meso*-(substituted)dipyrromethanes with a binary mixture of aldehydes according with the procedure previously described [42,43]. The precursor 1,2-dihydro-1,2-methanofullerene[60]-61-carboxylic acid was prepared according to the method described before in the literature [44]. To synthesize the diporphyrin dyads **3** and **4**, the carboxylic acid group of the porphyrin was transformed to acid chloride using thionyl chloride in dry toluene and pyridine. The acid chloride was immediately used for coupling with amino porphyrin [36, 41]. The porphyrin-C₆₀ dyad **5** was synthesized by a dicyclohexylcarbodiimide-mediated condensation of the C₆₀ carboxylic acid and the amino porphyrin [39]. All products were purified by flash chromatography column.

Photoelectrochemistry of Carotenoids Used in Artificial Photosynthesis

In order to analyze the participation of carotenoids in energy transfer and redox processes, it is necessary to explore conditions under which photophysics process of carotenoids can be elicited. Both the lowest excited singlet state (S₁) and the second excited singlet state (S₂) are of very short lifetimes: the S₁ decay time ranges from 50 to < 10 ps and the S₂ lifetime is ~200 fs [45-48]. In view of this fact, one way to overcome the kinetic limitations in artificial systems is to incorporate the carotenoid into a structure in which ultrafast photoinitiated reactions would be pseudo unimolecular. Thus, photoinduced electron transfer involving carotenoid compounds can be studied in organized assembly of the pigment in contact with a semiconductor electrode, where rapid electron transfer from the carotenoid excited state effectively competes with internal conversion [33-35]. We have reported the photoelectrochemistry of Langmuir-Blodgett films of synthetic amphiphatic carotenoids 7'-apo-7'-(4-carboxyphenyl)- β -carotene (ACC) [33] (**1**, Figure 2) and 7'-apo-7'-(4-aminophenyl)- β -carotene (H₂APC), [35] (**2**, Figure 2) showing that these polyenic molecules behaves as a photoconductor, and we have shown that upon illumination the synthetic carotenoids produce observable photocurrents in monolayer films in the presence of sacrificial electron acceptors.

The study showed that the synthetic carotenoids are able to form stable monolayers at an air-water interface and forms a photoactive electrode when are deposited on an ITO substrate. The match between absorption and photocurrent action spectrum implicates that the aggregates of carotenoid are the photoactive species. A suggested mechanism for the photocurrent starts with the transfer of an electron from the

excited carotene aggregate to benzoquinone sacrificial acceptor, followed by electron transfer from the conduction band of ITO to the hole in the aggregate (Figure 3). We reported a characterization of the photoelectrochemical behavior of the carotenoids based on the oxidation processes of carotenoids in solution [49-59] and in the solid state [60, 61]. The redox potentials are the basis for the calculation of the redox potential of the carotenoid excited states [1, 2], which drives sequential redox processes when organized films are deposited on the surface of semiconducting electrodes in the presence of external electron acceptors.

Our results further support the observation that carotenoid compounds can participate in electron transfer processes from their excited states when are included in organized assemblies and in close proximity to electron acceptors.

Photosensitization of Thin SnO₂ Nanocrystalline Semiconductor Film Electrodes with Supramolecular Organic Dyes

Porphyrin-Buckminsterfullerene Dyad (P-C₆₀)

An approach to mimic the photosynthetic energy conversion system in nature is the use of complex synthetic molecular arrays containing chromophores, electron donors and electron acceptors linked by covalent and non covalent bonds [62, 63]. The functionalization of C₆₀ buckminsterfullerene [64, 65] allows the linkage of this good energy and electron acceptor to many chromophores, and has opened the possibility of constructing artificial photosynthetic systems in which there is a photoinduced electron or energy transfer process from a chromophore donor to a fullerene acceptor. Thus, it is not surprising that great effort has been made in the synthesis and photophysical characterization of C₆₀ covalently and noncovalently linked to porphyrins, for which quantum yields of photoinduced charge separation state formation approaching to one have been reported [66-71]. Moreover, solid-state double-layer photoelectrochemical cells were developed using thin layers of solid C₆₀ and porphyrins [72], and showed that the photoinduced electron transfer from porphyrin to C₆₀ is the primary process of photocurrent generation at the porphyrin/C₆₀ interface.

Until the present, the photoelectrical studies of fullerene films demonstrated very weak activity, mainly due to the problems related to the construction of relatively thick films able to absorb most of the incident light [73]. Nevertheless, the properties of devices involving the generation of excited state of fullerene are still extensively analyzed due to their potential use in optoelectronic and photovoltaic applications. In our work we used a novel Porphyrin-C₆₀ dyad (dyad **5**, Figure 2) as light receptor in the spectral sensitization of nanostructured SnO₂ semiconductor electrode [39-41]. We obtained an efficient generation of photoelectrical effects from the excitation of both porphyrin and fullerene moieties in dyad **5**, and the formation of an intramolecular photoinduced charge transfer state $P^{+•}-C_{60}^{-•}$ was proposed, based on the following evidences.

The energy of the charge separation state in $P^{+•}-C_{60}^{-•}$ has been estimated from cyclic voltammetric experiments of the dyad **5** (Figure 4). The electrochemical reduction shows three one-electron processes, corresponding the waves I and II to the formation of mono and dianion of C₆₀ moiety respectively [74], and the last one (wave III, Figure 4) to the formation of porphyrin anion. On the other hand, oxidation of dyad corresponds to

the porphyrin radical cation (wave IV) and dication formation (wave V). The reduction and oxidation potentials of the dyad are similar to those of the combined individual monomeric units, and the results allow estimating the energy of the $P^{+•}-C_{60}^{-•}$ state, which is 1.43 eV above of the dyad ground state.

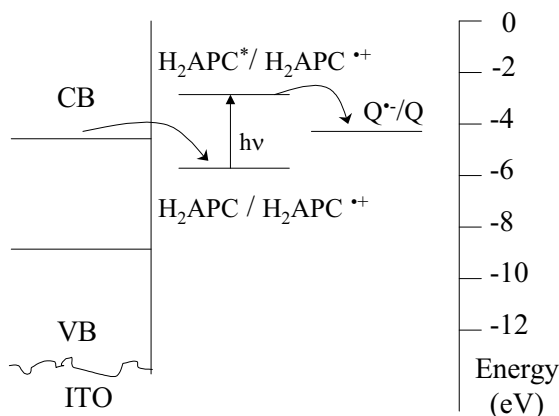


Figure 3: Carotenoid's generated photoelectric effect showed in a schematic diagram of the electron transfer processes. The arrows indicate the electron flow for the cathodic photocurrent.

On the other hand, the fluorescence emission spectra in toluene showed that dyad **5** produces a weaker emission from its porphyrin moiety (fluorescence quantum yield $\phi = 3.4 \times 10^{-3}$), in comparison with the porphyrine moiety, ($\phi = 0.19$) indicating a strong quenching of the porphyrin excited singlet state (quenching efficiency, $\eta_q \geq 0.98$) by the attached fullerene. Over the basis of our spectroscopies and electrochemical results we concluded that a photoinduced intramolecular electron transfer occurs in dyad **5** arising from $^1P-C_{60}$ state. AM1 calculation performed for dyad **5** (Figure 5) showed that the center-to-center separation is about 14 Å. This is distance larger than in those porphyrin-fullerene dyads where energy-transfer quenching of the porphyrin fluorescence was observed [75-77]. In these systems the strong electronic coupling between the moieties produce deformation and shift of the absorption bands in the UV-visible spectrum.

On the other hand, the incident-photon-to-photocurrent efficiencies (IPCE) for the ITO/SnO₂/dyad **5** electrodes were evaluated through equation 1 [78].

$$\text{IPCE (\%)} = 100 (i_{sc} 1240)/(I_{inc} \lambda) \quad (1)$$

where i_{sc} is the short circuit photocurrent ($A\ cm^{-2}$), I_{inc} is the incident light intensity ($W\ cm^{-2}$), and λ is the excitation wavelength (nm). After subtraction of the photocurrent response of bare ITO/SnO₂ electrodes, recorded before dye modification, the action spectrum for the dyad modified electrodes closely matches the absorption spectrum of the corresponding dye, as is shown in Figure 6. In contrast, the photocurrent spectra obtained with ITO/SnO₂/C₆₀ electrodes showed only small difference with those resulting from the band-gap excitation of the SnO₂ film, indicating that in these experimental conditions direct excitation of fullerene alone is not able to produce significant photoelectric effects [70, 80].

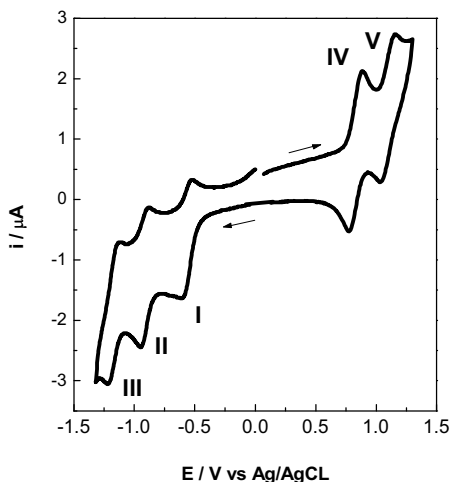


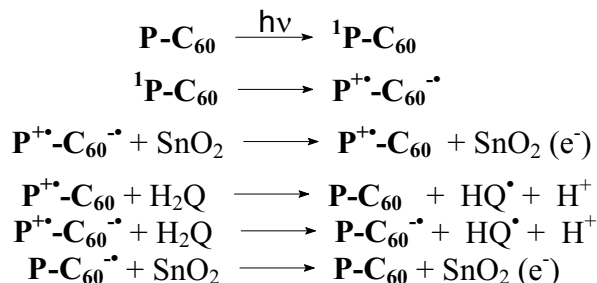
Figure 4: Dyad **5** cyclic voltammogram at a platinum electrode ($A = 0.031 \text{ cm}^2$) of 0.48 mM solution of dye in 1,2 dichloroethane containing 0.1 M Tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte, Sweep rate = 0.100 V/s.

In the action spectrum obtained with ITO/SnO₂/dyad **5** electrode, efficient generation of photocurrent at around $\lambda = 350 \text{ nm}$ is observed (Figure 6). This photocurrent is mainly produced by excitation of the C₆₀ moiety, as can be concluded from the analysis of the absorption spectrum of the dyad [81].

The charge injection yield (Φ_{inj}) from the excited dyes to the semiconductor times the charge collection efficiency, η_c , of the systems [12] can be obtained from IPCE and the light harvesting efficiency ($\text{LHE} = 1 - 10^{-A}$) of the dye, equation 2.

$$\Phi_{\text{inj}} \eta_c = \text{IPCE} / \text{LHE} \quad (2)$$

The product $\Phi_{\text{inj}} \eta_c$ in dyad **5** modified electrodes is around twice the one obtained with the porphyrin, despite the fact that in the dyad **5** most of the light is adsorbed by the porphyrin moiety. However, the lack of fluorescence from the porphyrin in the dyad **5** (both in solution and in adsorbed state) indicates that intramolecular charge transfer can compete with the electron transfer process to the semiconductor. Thus, we proposed that the photocurrent is being generated from the P^{•+}-C₆₀^{•-} photoinduced charge separation state [39-41, 82] as follows, where H₂Q represents the sacrificial donor hydroquinone present in the solution.



This mechanism precludes back electron transfer process (this deleterious process for the photocurrent efficiency would involve the reduction of the uncharged dyad), which showed to be the major limiting factor in achieving high IPCE values, producing low efficiency of photon to photocurrent conversion [83, 84].

Dyads Porphyrin-Porphyrin.

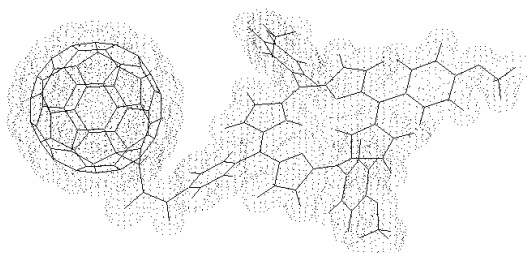


Figure 5: *Dyad 5 spatial architecture obtained by Austin Model 1 method.*

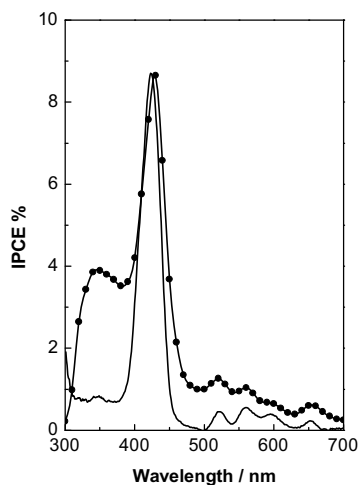


Figure 6: *ITO/SnO₂/dye 5 action spectrum as incident photon-to-current efficiency (---), and absorbance spectrum (—) of electrodes after normalization at the Soret bands.*

Like the photosynthetic reaction center, many artificial photosynthetic assemblies incorporate metalloporphyrins because they can be reversibly reduced and oxidized [85, 86]. Chlorophyll derivatives and several related porphyrins have been used as light receptors in energy conversion devices [15-24, 87-92], often in achieving spectral sensitization of wide band gap semiconductors. On the other hand, an “antenna-sensitizer” molecular device could be used in order to improve the overall efficiency of dye-sensitized solar cells [32]. In principle, this device would use intercomponent energy transfer from an “antenna” chromophoric unit to a specific chromoforic unit that behaves at the same time as an energy collector and as charge injection sensitizer.

In our studies first we have focused on a porphyrin dyad and its structural components (structure 3, Figure 2), as photosensitizing adsorbates on nanocrystalline SnO₂ films, in order to extend the photoresponse of this large band gap semiconductor

[36, 37]. This porphyrin dyad containing structural moieties with both different singlet state energies and redox properties can undergo singlet-singlet energy transfer or photo-induced electron transfer [93-99].

Nearly complete singlet-singlet energy transfer from the P_{Zn} to P has been observed in dyad **3**, both in solution and when the dye is in the adsorbed state over SnO_2 nanostructured photoelectrodes (Figure 7). On the other hand, SnO_2 films modified with porphyrin dyad and his moieties exhibit photoresponse in the visible region. The close match between the photocurrent action spectrum and the absorption spectrum showed that the photosensitization mechanism is operative in extending the photocurrent response of ITO/ SnO_2 /dye electrode to the visible (Figure 8).

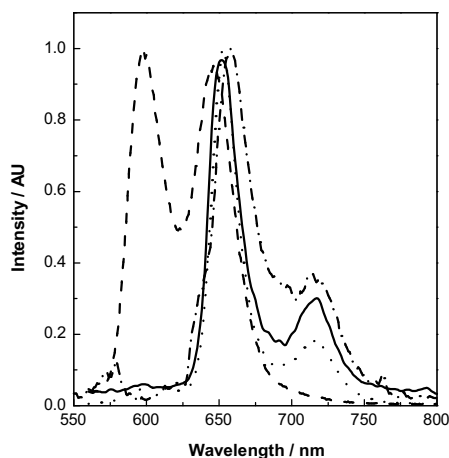


Figure 7: Corrected Fluorescence emission spectrum of P (—) and P_{Zn} (-----) moieties of dyad **3** in solution. Fluorescence emission spectrum of dyad **3** in both, solution (.....) and adsorbed over ITO/ SnO_2 / electrodes (- ·-) are also shown. $\lambda_{ex} = 550$ nm. The spectra have been normalized to one.

We found that the photocurrent efficiency in the dyad **3** and P_{Zn} are lower than P moiety, in spite of the fact that the E_{ox}^* value is more negative for the metallized porphyrin, which should facilitate the electron transfer from the excited state of the dye to the semiconductor. On the other hand, P_{Zn} is less efficient than P in the heterogeneous charge transfer process, but is a suitable energy donor, acting as “antenna” in the dyad **3** molecule. However, the photocurrent efficiency in the dyad was lower than the one produced by the free base moiety. This fact was explained considering that the metallized porphyrin enhances the back electron transfer process, producing low photocurrent yield [36-38, 100, 101]. We concluded that the lack of preferential orientation of the dyad over the SnO_2 surface (i.e., whether it is the free base moiety or the Zn-porphyrin moiety that gets attached to SnO_2 surface) play a role in determining the photocurrent quantum yield of the dyad [102].

In view of this fact, we designed and synthesized a new novel porphyrin-porphyrin supramolecular arrangement with particular structural and electronics properties. The asymmetrical dyad **4** (Figure 2) was designed in order to increase the intramolecular electron transfer capacity; one porphyrin moiety (P_{Zn}) bears electron-donating methoxy groups and a zinc ion, which help to stabilize the radical cation; the

second porphyrin moiety (**P**) features electron-withdrawing nitro substituent, which stabilize the porphyrin radical anion. Both moieties are linked by amide bond, which allows electronic interaction between the π systems of the two chromophores [103, 104]. On the other hand, dyad **4** bears a remnant carboxylic acid group on the **P** moiety. This group was conveniently located in the electron-withdrawing porphyrin moiety to benefit the orientation of the $\text{P}_{\text{Zn}}\text{-P}$ dyad on the basic semiconductor oxide electrode, in order to produce efficient charge injection and to keep the photooxidized porphyrin moiety away from the photoinjected electrons [38, 102].

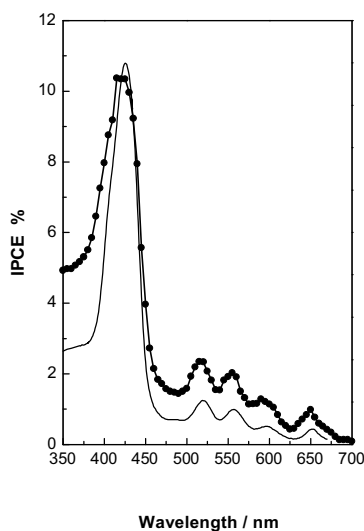


Figure 8: ITO/SnO₂/dye **3** action spectrum as incident photon-to-current efficiency (---), and absorbance spectrum (—) of electrodes after normalization at the Soret bands.

The photocurrent action spectrum and the absorption spectrum show that the photosensitization mechanism is operative in extending the photocurrent response of ITO/SnO₂/**4** electrode to the visible region (Figure 9), and demonstrate that the excitation of either moiety results in electron injection into SnO₂ conduction band, with similar electron harvesting capacity. It is proposed that, in the present case, the inhibition of back electron transfer is favored by the slower charge recombination kinetic in the $\text{P}_{\text{Zn}}^{+}\text{-P}^{\text{---}}\text{-SnO}_2$ (e) state with respect to the case where the oxidized cation is in direct contact with the semiconductor, producing higher photocurrent quantum yield than either component moiety. Moreover, fluorescence analysis of dyad **4** and his **P** moiety adsorbed on both SnO₂ and the insulator SiO₂ shows that the charge injection yield (Φ_{inj}) from the excited dye to the tin oxide semiconductor in both cases are similar [105]. Thus photocurrent enhancement is interpreted in terms of intramolecular electron transfer and preferential spatial orientation of the dyad on the tin oxide surface that preclude back electron transfer. The architecture of this dyad is a promising organic material for spectral sensitization of dye-semiconductor solar cells.

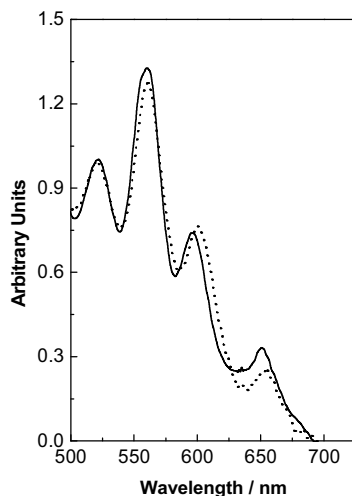


Figure 9: Normalized to one at 520 nm photocurrent (—) and absorption (-----) spectra of dyad 4 in Q band wavelength region (500 – 700 nm).

Conclusions

A new series of synthetic organic dyes has been used as light receptor in the generation of photoelectric effects. We demonstrated the participation of carotenoids compounds as excited state electron donors, and “antenna-effect” molecular devices were designed and used in order to improve the overall efficiency of dye-sensitized solar cells. Until now, the use of molecular system that mimics some aspects of the natural photosynthetic apparatus did not result in a commercial competitive energy conversion device, but progress in this area of research is impressive, and we are optimistic that the biological model will have a significant impact on the design and development of the next generation of solar cells.

Acknowledgments

The authors grateful acknowledge to the institutions that make possible the financial support of this research program: Secretaría de Ciencia y Técnica Universidad Nacional de Río Cuarto; Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET); Agencia Córdoba Ciencia; Agencia Nacional de Promoción Científica y Tecnológica, and Fundación Antorchas.

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