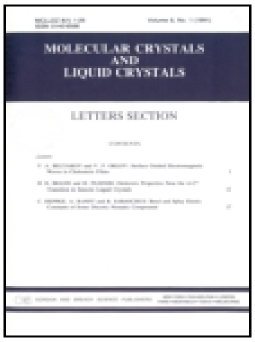

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# From natural photosynthesis to molecular photovoltaics

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**ABSTRACT**
In many technological applications the mankind mimics the nature. One of the excellent examples is photosynthesis. The knowledge of the natural photosynthesis mechanisms is extremely useful in understanding of molecular processes occurring in photovoltaics.
In this review article the photophysical fundamental aspects of photosynthetic units are presented. The similarity and dissimilarity between photosynthesis processes and photovoltaic ones is also shown. This paper is based first of all on the results of the investigations of corroles and corrole-fullerene dyads. The results of spectroscopic examinations supported by chemical calculations are presented.

**ABBREVIATIONS:** chlorophyll: Chl; bacteriochlorophyll: Bchl; ps: picosecond; fs: femtosecond; photosystem: PS; light harvesting complex: LHC; Langmuir-Blodgett: LB; reaction center: RC; dyes-sensitized solar cells: DSSC; fullerene $C_{60}$: C60; charge separation: CR; donor: D; acceptor: A; photoelectrochemical cell: PEC; N-4 methyloxybenzylidene-4-butylidine: MBBA; N-4 ethyloxybenzylidene-4-butylidine: EBBA; Förster resonance energy transfer: FRET; Langmuir-Blodgett: LB; Mg tetranaphtylporphyrin: MgTNP; Zn phthalocyanine: ZnPc; stilbene merocyanine: SM; electron spin resonance: ESR; infrared-reflection-absorption: IRRA; electron transfer: ET; energy transfer: EnT; dimethyl sulfoxide: DMSO; anthraquinone: AQ; Density Functional Theory: DFT

**KEYWORDS**
Photosynthesis; energy/electron transfer; organic dyes; corrole; fullerene

## 1. Introduction

The sun is the best renewable energy source. There are at least two available systems in which electron/energy transfer is the most important process in photosynthesizing organisms that turn solar energy into the carbohydrate products [1,2] and also in photovoltaic cells that convert solar light into electricity [3].

In many technological applications the mankind mimics the nature. In this review the fundamental aspects of mechanisms and processes occurring in photosynthesis which are also important in molecular photovoltaics are presented. The most beautiful and impressive example can be the phenomenon of photosynthesis and processes that take place in photosynthetic units after solar energy absorption. Since photosynthesis is the most efficient natural "device" it is very worth to mention about the light processes occurring in the photosynthetic systems

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The paper is dedicated to the memory of Professor Andrzej Graja (1940-2013)

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and to underline similarity between natural photosynthesis and photovoltaics (the later one very often named "artificial photosynthesis").

A dye solar cell was initiated by O'Regan and Grätzel for the first time in 1988 and it is known as a Grätzel cell. The results of the O'Regan and Grätzel studies were presented in Nature in 1991 [3]. Their studies opened a new era in the investigations of organic materials which can be used as photoactive agents in new generation photovoltaic devices. Since the end of the 20th century the performance of scientists has been developed extensively with the use of new photoactive sensitizers and made a great progress in studying, designing and fabrication of new photovoltaic equipments [3–12].

In the photovoltaic process extremely essential is to enhance effectivity of light energy into electric energy conversion with the use of organic dyes to ensure the proper functioning of a photovoltaic cell and its effective energy and electron transfer in an active donor (D) and acceptor (A) chain. To this day a lot of organic dyes like porphyrins, phthalocyanines and many others had been investigated. In a set of papers the results concerning both spectroscopic characterization of organic dyes and their ability to generate photocurrent in photovoltaic devices were presented [3–12]. Over last decades it was evidently shown that organic dyes (among them natural chlorophyll pigments) are able to produce photocurrent in a variety of dyes-sensitized solar cells (DSSCs) [3–12]. Low production cost and easy disposal make organic dyes very attractive materials for solar conversion. The DSSCs can be composed of a proper layer of semiconductor (usually $TiO_2$, ITO, $In_2O_3$) with a layer of a dye that absorbs incident light. However, extremely important problems which have been arrived in tailoring of DSSCs are low stability of dyes, short diffusion pass-way in a dye layer, fast charge recombination process and consequently low efficiency of light energy to electric energy conversion.

Thus, the main venture for researches is searching for various solar cell architecture and new organic dyes that are expected to be very good agents for DSSCs. Until now, a lot of studies have been directed towards new organic dye systems which are expected to find application in the future as very good materials characterized by fast energy transfer, slow charge recombination and sufficient photostability.

In this review article attention is concentrated on a family of fairly new corrole dyes and their covalent dyads with fullerene $C_{60}$ (C60). The most important results of the spectroscopic studies of selected corroles and their dyads with C60 are presented. Spectroscopic properties were determined with the use of a variety of experiments in solution and in Langmuir-Blodgett (LB) nanolayers. The experimental data have been supported by the quantum calculations.

## 2. Light reaction in photosynthesis

### 2.1. *The principles of photosynthesis*

Photosynthesis organisms (plants, algae and photosensitizing bacteria) in which chlorophyll (Chl) or bacteriochlorophyll (Bchl) pigments and other complementary ones operate as light harvesting agents to absorb solar energy [2]. Absorbed energy is transferred between pigments to a special pair (Chl or Bchl dimers) localized in the reaction center (RC) [2,13]. Photosynthesis is the excellent representative of the best and very efficient photovoltaic systems in the nature [2]. The special pair is responsible for the charge separation (CR) process. In the RC an excited special pair serves as a primary electron D in the D-A chain. An electron is being transferred across a pigment-protein-lipid membrane and afterwards the transferred electrons are used in chemical reactions leading to carbohydrate production in the last chemical stage [1,2]. Some proteins (called pump proteins) use their oxidation-reduction power to transfer protons from one side of a membrane to the other side and create the light-potential gradient between the opposite sides of the membrane. This phenomenon has been investigated by many authors [2,13–15]. Typical values of membrane potential range from −40 mV to −80 mV depending on a kind of photosynthesizing organism.

On the molecular level the photosynthesis process can be described as widely known equation:

$$DA + h\nu \rightarrow D^{*}A \rightarrow D^{+}A^{-} \tag{1}$$

where D and A are a donor and an acceptor, respectively, $D^{*}$ is excited D molecules, $D^{+}$ and $A^{-}$ are oxidized and reduced D and A, respectively.

As mention above the main processes occurring in the photovoltaic effects both in the natural and artificial systems is energy and electron transfer occurring after light absorption. How important is the knowledge of molecular mechanisms of electron/energy transfer and charge separation in a molecular membrane as well as of light-gradient generation is evidenced by numerous papers (some selected papers [2,13–16]). Thus, it is very essential to follow the primary photophysical processes occurring in the photosynthesizing organisms as well as properties and function of chlorophyll pigments to get knowledge on energy/electron transport phenomena.

The particular complexes of plants and photosynthetic bacteria are light-harvesting systems that are a part of the functional unit in photosynthesis and they collect incoming light. The light-harvesting complexes consist of proteins and photosynthetic pigments. They surround the photosynthetic RC and energy absorbed by pigments in the light-harvesting systems is transferred by the Förster resonance mechanism to reach a Chl or Bchl dimer. From our view point the most essential processes occurring in photosynthetic organisms take place immediately after light absorption. The function of light harvesting complexes is to capture photons by antenna pigments and excite the Chl/Bchl singlet state. The light-harvesting complexes are specifically localized in a membrane to optimize interaction and the rates of energy transfer. The excitation can be deactivated by radiative processes (fluorescence), non-radiative processes (thermal deactivation), chemical reactions and exciton-exciton annihilation. The next stage of the light reaction process is energy trapping in RC where charge separation occurs in the special pair – Chl (or Bchl) dimer which is a primary electron donor. Then the electron is transferred to the intermediary acceptor and by pheophytin to a first stable acceptor – a type of quinone to form finally the light gradient across the membrane. The schemes of natural photosynthetic unit, light-harvesting complex and reaction center models are shown in Fig. 1.

The light reactions are extremely fast; the excitation of the light-harvesting pigments takes about femtoseconds (fs) – in the RC the radical pair is created in about 1–3 picoseconds (ps) [2,14,15]. After the charge separation process an electron is transferred from the excited Chl dimer through the chain of intermediary electron carriers to the final acceptors and light gradient is created across the membrane.

Purple and green bacteria are the simplest living organisms that are able to make photosynthesis [2,13–15]. The high-resolution molecular structure of the bacterial reaction center is very well known and was elucidated with the use of X-ray crystallographic analysis by Diesenhoffer *et al.* [17]. Their structures are much less complexes than those of plants – bacteria

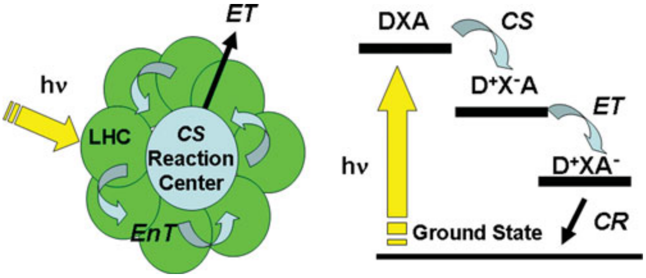

**Figure 1.** Models of energy and electron transfer in photosynthetic unit (left) and of electron transfer in photovoltaic device (right); LH – light harvesting complex, ET – electron transfer, EnT – energy transfer, DXA – donor-X-acceptor chain, CS – charge separation, CR – charge recombination.

possess only one photosystem. Therefore, in many investigations the models of photosynthesis bacteria can be applied to follow energy and electron transfer processes [14,15]. A perfect example of photosynthetic electron transfer process in the RC of the purple photosynthetic bacterium *Rhodobacter sphaeroides R-26* is presented in [14,15]. The studies of Bchl (800 nm excitation) showed characteristic multiphase absorbance changes with the use of transient absorption spectroscopy of a time resolution 120 fs at room temperature. These changes were assigned to the appearance of a primary donor (Bchl dimer) and an acceptor (bacteriopheophytin) [15]. A signal appeared within 120 fs was assigned to oxidized Bchl (at 600 nm). The electron transfer to the bacteriopheophytin acceptor (in 3 ps) was also shown. Then, the electron from the reduced bacteriopheophytin (detected at 546 nm and 670 nm) was transferred to a quinone acceptor in about 200 ps and it was observed as the intensity changing in the transient absorption bands.

Green plant organisms are more complex and they are composed of two units called photosystem I (PSI) and photosystem II (PSII) cooperating effectively in energy and electron transfer processes [2,13–16,18]. The light-harvesting complex of PSII LHCII is the principal solar energy collector and it is responsible for the efficient light-harvesting process in which both Chl *a* and Chl *b* take place [1]. The complementary carotene pigments function both as a harvesting agent and also as a system that protects, due to non-radiative deactivation, against high light exposure damage of absorbed solar energy [2]. The structure of photosystem II was reported at a resolution of 1.9 Å and the results helped to analyze and understand functions of the photosynthetic units in energy and electron transport [16,19].

The general function of plants and other photosynthesizing organisms is to capture solar energy and also to convert sunlight, $CO_2$ and water into carbohydrates. Determination of the relative efficiency of photosynthetic process is not a simple problem. Solar (or light) energy absorbed by a plant is dissipated in non-radiative processes (e.g. as heat) to avoid damaging in apparatus. The energy is also being lost in radiative decay processes (emitted as Chl fluorescence) or in other ways. Only 40–45% of the sunlight is in the active energy range and the theoretical maximum efficiency of solar energy conversion is approximately 11% and nominal efficiency is 30% [1,2]. Photosynthesizing organisms do not absorb all incoming solar radiance and do not convert all harvested energy into biomass. Thus, it results in the overall photosynthetic efficiency of 3 to 6% [1,2]. According to the model proposed by Wasielewski the number of electrons transferred to molecules in RC in the photosynthetic units to the number of absorbed photons is almost 100% [20]. This model evidently confirms that the photosynthesis system is a perfect “device”, which is able to convert light energy into electric energy with extreme efficiency.

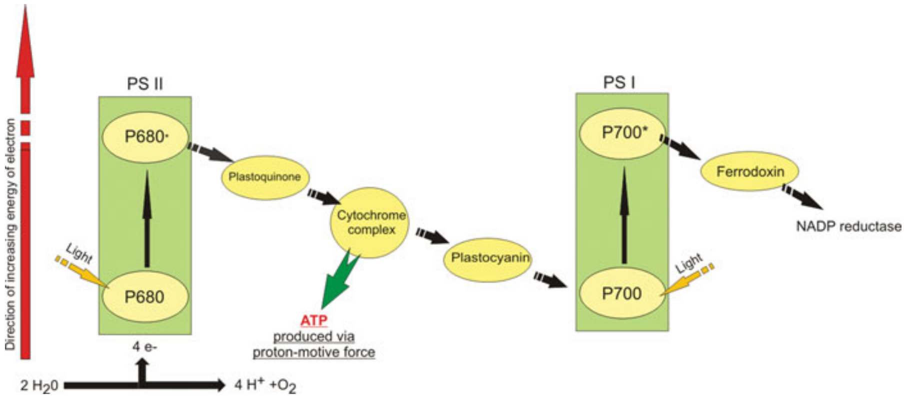

**Figure 2.** Z-scheme of electron transport in photosynthesis.

## 2.2. *From natural to artificial photosynthesis*

Electron transport in photosynthesis can be well presented with the use of the Z-scheme. Its many versions were presented in specialist papers and have been developed over decades [e.g. 1]. The Z-scheme presents an electron-donor-acceptor pass-way in photosynthesis of the PSII and PSI systems in green plants that were studied by many investigators. First of them was Emerson who showed that in green plants two photosystems (currently called PSII and PSI) have to cooperate by light absorption at different wavelengths simultaneously (670 nm and 700 nm) and the rate of photosynthesis is much higher than that of the red light and far red light rates (Emerson enhanced effect [18]). The Z-scheme is shown in Fig. 2 and it concerns the redox reaction in PSII and PSI. An absorbed photon excites Chl II, and then an electron is transferred by light-harvesting species to the RC dimer (the left side). In the RC charge separation takes place and an electron is transferred to more reducing species in the electron D-A chain. Then, the electron donates Chl I (the right side) and it is used in chemical reaction leading to the final product. The primary D of an electron is water split by solar excitation to replenish the electron taken from Chl. In this pathway photosynthesizing organisms transform light energy into electrical energy.

A fragment of the photosynthesizing apparatus of the green sulfur bacterium *Prosthecochloris aestuarii* and Chl *a* may be the excellent examples of a link between natural and artificial photosynthesis [21,22]. Fig. 3 shows the results of the experiments confirming the ability of an bacterium cell and Chl *a* to generate photocurrent. The mechanism responsible for photocurrent generation was assigned to electron injection from an excited pigment (or other molecular materials) to a semiconductive electrode. A metal electrode replenishes the electron extracted from a molecular material. Fig. 3 A shows the kinetics of photocurrent generated in the fragment of the bacterium sample in a photoelectrochemical cell (PEC); PEC is made of metal (gold) and semiconductor ($In_2O_3$) electrodes ($In_2O_3$/sample/Au) [21]. After lighting off, a non-exponential signal decay is observed. The photocurrent origin results from at least two effects: the effect of the rapid process occurring immediately after photons absorption associated with charge separation in the RC, and the slower process resulting from migration of charges in the degenerate antenna dyes. The action spectrum (photocurrent dependence on excitation light wavelength) and the shape of the curve confirm that Bchl is responsible for generated photocurrent [21]. The results presented in [21] and their interpretation was consistent with the results received by Shulachev [23]. Shulachev showed that in purple bacteria the value of potential generated by the antenna pigments was one order

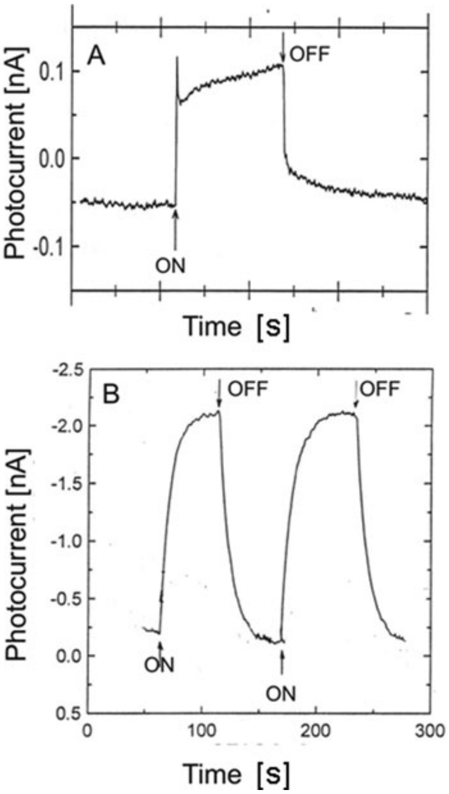

**Figure 3.** Kinetics of generation and decreasing photocurrent of *Prosthecochloris aestuarii* fragments (A), photocurrent generation of Chl *a* (B) in PEC ($In_2O_3$/sample/Au); 150 mW/cm$^2$. Chl *a* in MBBA+EBBA ($10^{-3}$ M). ON – light on, OFF – light off; (courtesy of A. Ptak).

less than that of the potential resulting from the RC. Chl and Chl-like pigments belong to a porphin family and they may be representative dyes in photovoltaics as photoactive molecular materials. Because of Chls are the most important pigments in the natural process of photosynthesis selected results obtained by Ptak et al. [22] are presented. Fig. 3 B shows the results of the experiments done for PEC filled up with Chl *a*. The mechanism responsible for photocurrent generation is electron injection from the excited pigment to a semiconductive electrode. A metal electrode completes electrons extracted from Chl. The results showed the ability of Chl *a* to generate current in a sandwich cell build-up with the use of the semiconductor ($In_2O_3$) sprayed on a sodium-calcium plate and with a gold electrode. The kinetics of photocurrent of Chl *a* dissolved in a nematic liquid crystal (N-4 methyloxybenzylidene-4-butylidine + N-4 ethyloxybenzylidene-4-butylidine - MBBA+EBBA) is shown (Fig. 3 B). The experiments done by Ptak [22] and other authors who confirmed the results both of the bacterium fragments and of Chl *a* in PEC are the evidence of the ability of photosynthetic materials to generate electricity.

## 3. Energy and electron transfer processes in photosynthesis and molecular materials

Energy and electron transport processes are exceptionally impressive both in photosynthesis and photovoltaics. One of the most important keys in tailoring new optoelectronic devices is the knowledge of energy and electron transfer processes occurring in photosynthesis systems. Thus, the knowledge of the basic processes and their mechanisms can be very useful in studying, developing and proper designing photovoltaic devices based on light absorbing photoactive organic materials.

The investigations of the photophysical processes occurring in the photosynthetic units are also extremely useful in getting knowledge on the mechanisms responsible for light-gradient photovoltage creation. Contribution of dyes and their dyads in energy and electron transfer is also the point of many studies [24–30]. Phenomena and processes essential for high effectiveness of optoelectronic devices based on molecular systems include: strong $\pi$-$\pi$ light absorption, efficient energy transfer between D and A, fast electron transfer in a D-A chain followed by charge separation and slow charge recombination [31,32]. The mechanism of the excitation energy transfer process was proposed for the first time by Förster [33]. Förster long-range resonance excitation energy transfer (FRET) [34] is useful in studying interaction in a D-A unit distanced in the nanoscale range. According to the Förster theory the interaction between D and A can be approximated by the dipole-dipole interaction. The rate of energy transfer is expressed as follows:

$$k_{EnT} = \left(\frac{1}{\tau_0}\right)\left(\frac{R_0}{R}\right)^6, \tag{2}$$

and it depends very strongly on donor lifetime ($\tau_0$) and the A-D distance R. The $R_0$ is the Förster distance (the Förster radius) of the D-A pair at which the energy transfer efficiency is 50% and it is expressed:

$$R_0 = \left(\frac{C\kappa^2}{n^4\tau_0}\right)\int \frac{F(\nu)\varepsilon(\nu)}{\nu^4}d\nu, \tag{3}$$

where: $\kappa$ is the dipole orientation factor that describes the mutual orientation of the D emission dipole moment and the A absorption dipole moment, F($\nu$) and $\varepsilon(\nu)$ are fluorescence and absorption over the $\nu$ light frequency, respectively. The EnT parameter can be evaluated with the use of eq. 4:

$$\Phi_{EnT} = \left(\frac{R_0}{R}\right)^6 \Big/ \left[1 + (\frac{R_0}{R})^6\right]. \tag{4}$$

The energy transfer process described by Förster model takes place when the distance between D and A ranges from about 10 Å to about 100 Å.

When the energy of interaction between D and A is greater than the width of the transitions (e.g. a case of strong coupling interaction when the separation in the D-A pair is much closer ($R \leq 5$ Å)) the energy transfer process can be described with the use of the exchange mechanism proposed by Dexter [35]. The strong coupling interaction also requires overlapping of the D and A wave functions. The excitation is delocalized over D and A and oscillates back and forth between them. The fluorescence lifetime of D is of the order $10^{-8}$ – $10^{-9}$ s. The energy transfer rate constants can range from $10^9$ to $10^{14}$ $s^{-1}$ depending strongly on a type of systems and mechanism responsible for the process. Fig. 4 A and B shows the simplified Förster and Dexter models.

The electron transfer (ET) theory was originally proposed by Marcus in 1956 [36]. The simple model of ET can be presented as $D + A \rightarrow D^+ + A^-$. Marcus model has been developed through a few decades [37] to explain the outer ET from D to A in two individual and not directly linked species. The theory was then extended to the inner ET model [37 and citations herein] in which two chemical species are linked chemically. In the Marcus theory the

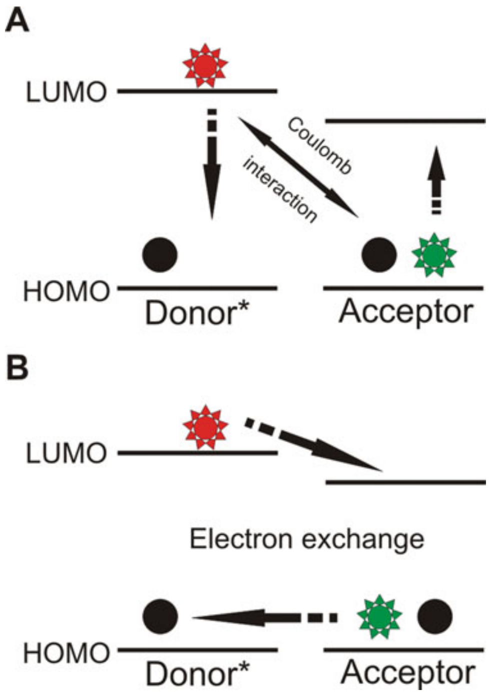

**Figure 4.** Simplified models of FRET (A) and of exchange Dexter (B) mechanisms.

rate constant for electron transfer is expressed by eq. 5:

$$k_{ET} = \frac{2\pi}{\hbar}|H_{AB}|^2\frac{1}{\sqrt{4\pi\lambda K_b T}}\exp\left(-\frac{(\lambda+\Delta G)^2}{4\lambda K_b T}\right), \tag{5}$$

where: $H_{AB}$ is the electronic coupling between the initial and final states, $\lambda$ is the reorganization energy, $\Delta G$ is the total Gibbs free energy change for the transfer reaction, $K_b$ is the Boltzmann constant, $T$ is absolute temperature. The energy reorganisation $\lambda$ is a sum of internal energy $\lambda_i$ (connected with changes in molecular geometry at the transition from the neutral molecule to its ion) and energy of outer reorganisation.

## 4. Molecular organic materials for photovoltaics

The fundamental advantage of organic materials like e.g.: simplicity in chemical treatment, low costs of production, straightness in utilization, appropriate spectral parameters as well as sufficient effctivity in electron separation and weak charge recombination is an additional motivation to thorough search and investigate suitable materials.

In the first dye-sensitized photovoltaics photoactive molecules were sensitive to the UV and blue light [24,25,38–43], however over the past few decades intense studies brought a great evolution in cell designing with the use of a series of $\pi$-electron dyes and their complexes as photosensitizers to improve DSSC. Among them there are cells based on porphyrins, phthalocyanines and other macrocyclic dyes absorbing intensively in the light visible range [41–46]. The first successful solid-hybrid dye-sensitized solar cells were reported to improve electron transport [47]. Numerous research groups experimented with a wide variety of photoactive materials [26,40–43,48–52]. Many new dye-sensitized solar cells based on organic functional dyes comprised of porphyrins covalently linked to other moieties such as thiophenes building blocks, rhodamine or ruthenium complexes were also extensively reported as photosensitizers for developing photoelectrochemical solar cells [41,43]. Also porphyrin-sensitized $TiO_2$ or systems with porphyrin-gold nanoparticles [42] were demonstrated as suitable materials. The various research groups presented the results of the chromophore-based DSSC devices with the different working media: from traditional organic liquid electrolytes, ionic liquid electrolytes, polymer gel electrolytes, quasi-solid state to self-assembled monolayer Schottky barrier cells, and other systems [42,43,53,54]. In many cases these systems offer high photovoltaic effect, chemical and thermal stability and developing long-term solar cells. Basic spectroscopic properties of photoactive dyes and correlation between the molecular structure of dyes and their ability to photocurrent generation were also the subjects of many studies [40–54].

In photosynthesis a kind of quinone acts as electron A. Thus, photoinduced ET in a mixture composed of free-based and selected metal-complexed porphyrins and anthraquinone (AQ) in dimethyl sulfoxide (DMSO) were also investigated. The quenching of dye fluorescence in the presence of AQ was reported as a process characterized by the bimolecular quenching rate from $0.7 \cdot 10^{13}$ to $13 \cdot 10^{13}$ $M^{-1-1}$ and with the ET rate constants estimated as $0.36 \cdot 10^9$ $s^{-1}$ - $0.36 \cdot 10^9$ $s^{-1}$ depending on the studied dyes [52].The light-induced electron spin resonance (ESR) signals supported the fluorescence quenching data. The observables were discussed as originating from the electron transfer in the porphyrin-AQ pair from the porphyrin singlet excited state to the AQ molecule. It leads to formation of radical ions and charge recombination processes [52]. The analogue examinations of porphyrin-quinone mixtures and also porphyrin-quinone dyads were described also in [55–58].

The correlation between the molecular structure of selected porphyrins (or phthalocyanines) and their ability to generate photocurrent was followed by absorption spectroscopy and photovoltaic responses in PEC [44–46,59–63]. A coincidence of the observed absorption and photovoltaic action spectra of the investigated porphyrins confirmed responsibility of the dyes for the photovoltaic signals [52]. The intensity of photocurrent generated in the PEC based on porphyrins or phthalocyanines was shown to be dependent of a kind of metal ion complexed with free-base dyes due to its ability to change distribution of the $\pi$-electrons; it was observed that the presence of Mg or Zn in the center macrocycle leads to photocurrent enhancement [64]. Also peripheral groups like aromatic rings attached to the porphyrin rings or to the phthalocyanine indole units are able to affect positively the current intensity value [64]. Also the presence of aromatic rings or atoms (e.g. fluorine, chlorine) attached to the porphyrin or to the indole in macrorings usually enhance photoresponse due to higher number of $\pi$-electrons and their delocalization [44–46]. Otherwise, the long alkyl or alkyloxy chains in dye molecules cause diminishing current response since absorbed energy is released in non-radiative processes [64]. The influence of mesomeric, inductive and steric effects on photocurrent generation were also discussed [44].

The artificial models can use either one type of dye with a broad absorption range or a system of several dyes immersed in an artificial system [65–69]. The results of photocurrent generation in a mixture of good photoconverters (Mg tetranaphtylporphyrin (MgTNP) with Zn phthalocyanine (ZnPc)) or with a poor photoconverter (stilbene merocyanine - SM) were also reported [64]. The SM fills up the energy gap of the spectrum of a porphyrin and phthalocyanine mixture in a wide solar range The photocurrent generated in PEC with the SM and MgTNP mixture is markedly enhanced due to efficient FRET between the dyes. In contrary, the decreasing photoresponse (with respect to that of the individual dyes) is observed in PEC with the MgTNP-ZnPc mixture as a result of high thermal relaxation of dye aggregates in PEC [64]. On the other hand, a mixture of weak electron-donating 5,10,15,20-tetra(2,5-dimethoxyphenyl)porphyrin and a weak electron-accepting metal-free 5,10,15-triphenyl-20-(3-pyridyl)porphyrin was shown to be more efficient in photosignal generation with respect to the individual species [70], However, the usefulness of larger arrays including mixed systems with many components absorbing in the overlapped light range was presented [71]. The optimisation of porphyrin light harvesting systems of highly ordered architecture in the form of columns kept by the intermolecular $\pi$-$\pi$ stacking was also shown [e.g. 72].

In the last decade photoactivity in photocurrent generation of various types of photovoltaic devices with different working media (fulfilled with porphyrins, phthalocyanines and other chromophores of different molecular structures, porphyrin-inorganic particles ($TiO_2$, gold, quantum dots) or functionalized building blocks and cells of different architecture) were intensively studied by numerous authors [65,66,70–72] for developing photoelectrochemical solar cells.

## 5. Corroles and fullerenes

### 5.1. *Basic properties of corroles*

Many researchers and development centers and groups of physicists and chemists and other research workers involved in material synthesis concentrate on modeling and solving problems to improve solar cell design and effectivity. However, the efficiency of some systems proposed in [25,26,38–42] is still too low to fulfill current technical and economic as well as ecological requirements. Therefore, it is very essential to find new molecular materials, which are characterized by not only strong light absorption in the range of the maximal solar exposure but also by fast charge separation and slow charge recombination.

So far, photophysical properties of corrole dyes are not sufficiently known and therefore they require further research for their application. In that regard, great expectations are connected with corroles – one carbon-less analogues of porphyrins. Corrole dyes are aromatic macrocycles structurally similar to porphyrins; they are one carbon-less analogues of porphyrin dyes [73]. The simplified molecular structures of the free-based corrole and free-based porphyrin are shown in Fig. 5.

The corrole structure differs from that of porphyrin in a direct pyrrole-pyrrole linkage resulting in the reduced symmetry, a smaller cavity, and the ability to support higher oxidation states. In particular, they possess stronger absorption in the red light region compared to some porphyrins, have much higher fluorescence quantum yield, larger Stokes shift, lower first oxidation potentials and entirely different coordination chemistry [74]. The UV-vis spectroscopy study of corroles showed clearly an intense Soret band and less intensive Q bands [74]. Moreover, corroles are more acidic than porphyrins and they are easier to oxidize and more difficult to reduce [73,75]. Corroles have also several differences in comparison to porphyrins: lower symmetry ($C_{2V}$) due to missing one *meso* carbon bridge, the ring of corrole is smaller and thus there is slightly less space in the middle resulting in metal sitting slightly out of the plane. In consequence, the differences can result in strong changes in photophysical and photochemical properties. These properties of corroles open the way for using them to particular application in DSSC.

The first synthesis of corroles was reported by Johnson and Kay in 1965 [73]. However, they have not been a subject of investigations for over more than 40 years due to the difficult chemical synthesis. The beginning of the 21th century opened a new area in the modern chemical procedure and let improving and developing the new branch of corrole chemistry [76,77].

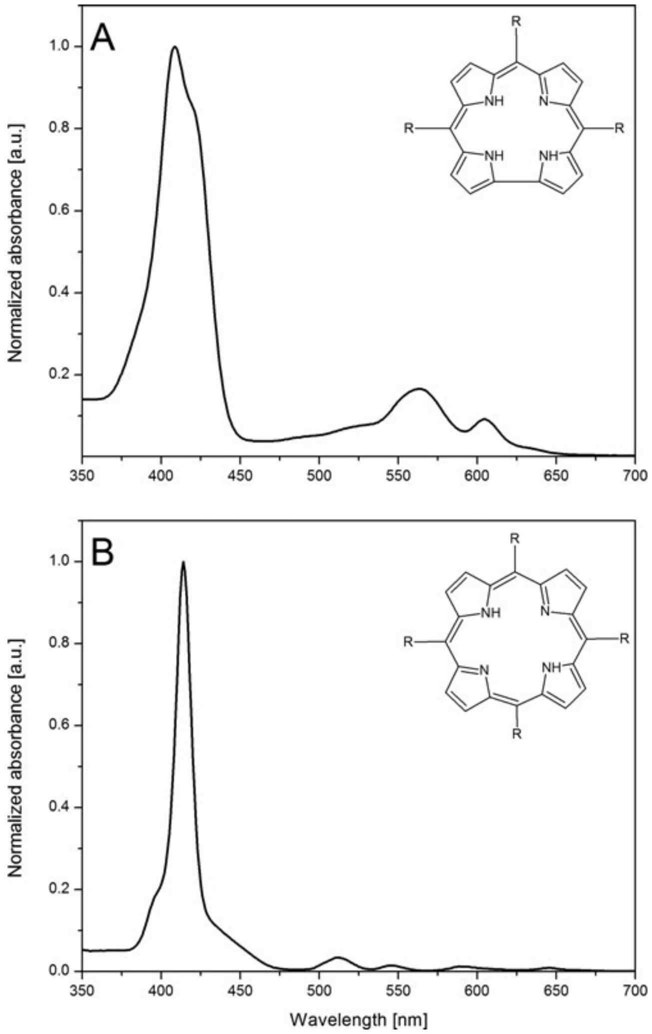

**Figure 5.** Simplified models of the molecular structures of free-base corrole (A) and free-base porphyrin (B) and their absorption spectra in solution.

The previous studies revealed that covalent dyads with fullerenes possess relatively long lifetime of the charge-separated state [24,25]. In [74,78] it was presented self-organization of *meso*-substituted corroles possessing secondary amide groups. Depending on substituents, corroles can form head-to-tail dimers or larger moieties. The structural diversity of potential corroles motives and allows obtaining new structures of new types. Imahori and Fukuzumi and co-workers presented the long lifetime of the charge-separated state in chlorine porphyrin and fullerene units. The charge separation is due to electron-transfer operating in a Marcus inverted region and it is closely related to a small distance between two units [27]. Imahori et al. also reported the long charge separation time in ferrocene-porphyrin-fullerene units [24,25].

More and more interests are various super- and supramolecular covalent and non-covalent systems [68 and references herein, 63,79–90]. However, it is still very little known about corroles and their covalent dyads with fullerene. Thus in the chapter presented below the selected results comprising assorted corroles and fullerene $C_{60}$ to characterize and to follow processes occurring in the corrole-carbon systems by the use of the complementary experimental methods supported by the quantum-mechanic calculations are presented.

### 5.2. Corroles and fullerene dyad as an example of electron donating-withdrawing systems

The studies performed by Graja and a group co-working with him in the last few years will be pointed out. The main topic of the studies was corroles and corroles covalently linked to fullerene. As said above, corroles dyads with fullerenes possess long lifetime of the CR state [24,25]. Thus, they can be promising materials for composition with fullerene C60, because C60 is able to link electron-donor chromophores and to create a supermolecular complex. The C60 is a 3D system of conjugated linkages ($\pi$-electrons), a perfect electron A and it is chemically and thermally very stable material. In addition, fullerene is a material with a very low energy reorganization. In some corrole-fullerene dyads investigated by D'Souza et al. the reorganization energy values are estimated as 0.51- 0.71 eV depending on solvent polarity [77] and the CS rate ranges from $10^{10}$ to $10^{11}$ s-1. Also the charge transfer process and energy reorganization of porphyrin-fullerene complexes were investigated [79]; the reorganization energy value in a porphyrin-fullerene dyad in benzene is about 0.23 eV [79].

This paper is focused on the results concerning spectroscopic investigations of corroles and interaction of corroles with fullerene in covalent complex [91–98]. In one of Graja's papers [96] he asked the question *Corrole-fullerene dyads - will they replace porphyrin-fullerene systems?* and he discussed the arguments supporting corroles as photoactive dyes as species good enough for photovoltaics. He also presented some arguments against them. Many experimental methods were performed to follow spectroscopic properties of corrole-fullerene systems and processes occurring after irradiation. The samples were studied in solution and in Langmuir-Blodgett (LB) nanolayers on solid substrates. The experimental methods with the use of unpolarized and polarized light were: UV-vis-IR absorption, steady-state and time-resolved fluorescence, IR reflectance-absorption (IRRA) and IR photoacoustics. In order to interpret the experimental results the quantum chemical calculations (Density Functional Theory – DFT; B3LYP hybrid functional with the 6–31G basis)) method was used to supply the experimental data. The samples under studies are an individual chromophore fluorine–substituted free-based corrole and a dyad consists of the corrole covalently linked to C60.

When the corrole dye was linked to C60 no particular changes in the shape and location of the maxima were observed [92]; the maxima locations were shifted about 1–2 nm in the whole UV-vis absorption range. This result confirmed rather week interaction of the corrole with C60 in the electronic ground state. The corrole is characterized by strong emission originating from the $S_1$-$S_0$ transition [77] – it is shown in Fig. 6 A – the maximal high intensity at about 652 nm was observed. The interaction between the corrole and C60 was radically changed after excitation (Fig. 6 A and B). The quenching of corrole fluorescence in the presence of C60 was interpreted as due to efficient ET from the chromophore to the fullerene. The evaluated values of the fluorescence quantum yield of the corrole *versus* the corrole-fullerene unit decreases from 10% to about 3.5% and fluorescence life-time from 3.80 to about 1.00 ns (90% weight) and reaffirmed the strong ET from the corrole to the fullerene species. The quantum yield of the electron transfer was evaluated as about 60–70% [92]. For more detailed information on fluorescence quenching of the investigated corrole in the presence of C60, the time dependent density functional theory (TD-DFT) calculations of transition energies were performed for the dyad [92]. Fig. 7 shows the results and it acknowledges the electron density distribution in the investigated systems in the HOMO and LUMO energies. In the corrole the

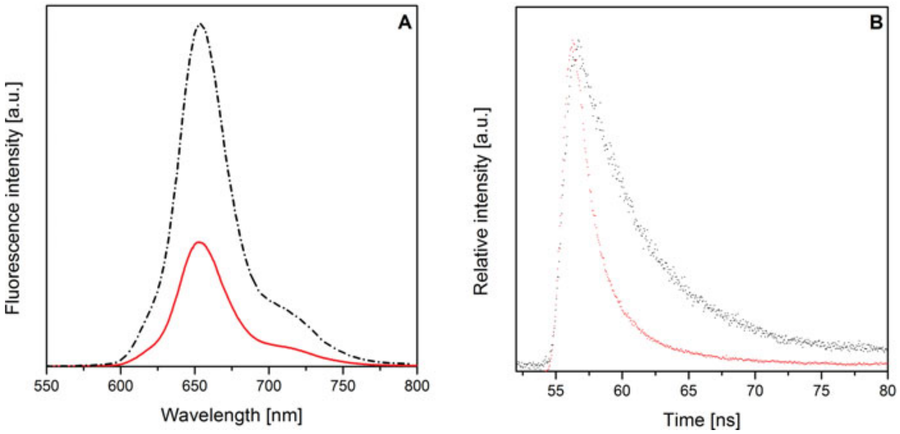

**Figure 6.** Fluorescence spectra of corrole ($10^{-5}$M) and corrole-fullerene in chloroform (A) and their appropriate kinetics (B); exc. 405 nm; (based on [91]).

HOMO was localized on the macroring and the localization of the LUMO remained almost the same. In the corrole-C60 moiety the LUMO was localized mostly on the fullerene and not on the corrole microring.

The electron density is high in the corrole (HOMO and LUMO) and in the corrole-C60 (HOMO). In the corrole-C60 in the LUMO state, it is not on the corrole microring [92, also see also table herein]. The TD-DFT results strongly confirm that the HOMO is localized on

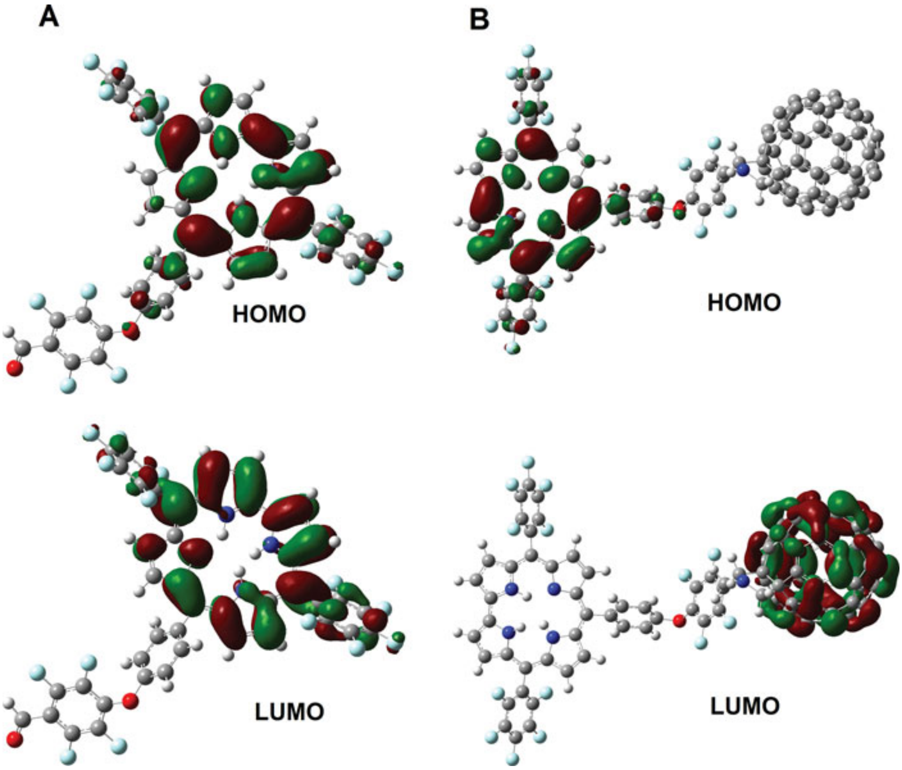

**Figure 7.** Model of electron density distribution in corrole (A) and corrole-fullerene dyad (B) (courtesy of B. Barszcz).

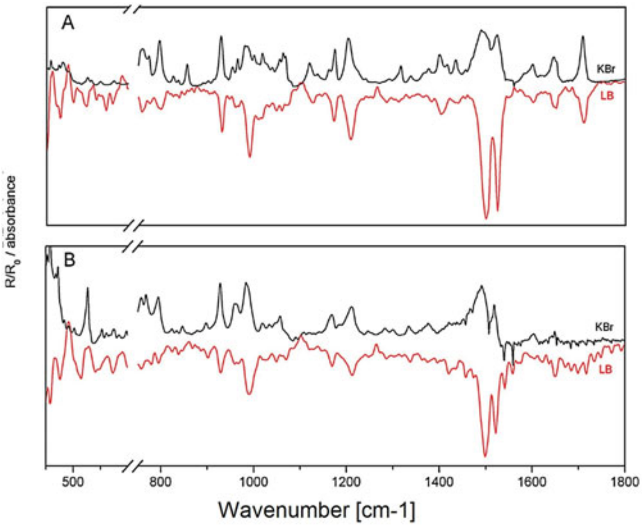

**Figure 8.** IR spectra of corrole (A) and corrole-fullerene (B) in KBr and FT-IR reflection- absorption spectra in p-polarized light of corrole (A) and corrole-fullerene dyad (B) in LB layers.; 5 LB layers on a gold plate; incidence light beam —$80^0$ (based on [91]).

the corrole $\pi$-electrons and the LUMO on the fullerene. These results are in good agreement with D'Souza paper [77].

One of the first porphyrin-fullerene systems was ferrocene-zinc-porphyrin-free-based porphyrin-fullerene and it was presented by Imahori et al. [30]. Guldi [29] and Imahori [28,30] investigated lifetime of the charge separated state. It was shown that the D-A distance, fast and efficient ET and the long-lived CS state can only be reached in a short range [28,29]. Porphyrin-fullerene-linked triads and tetrads display multi-step ET, mimicking the primary CS in the photosynthetic RC. In the triad and tetrad the high ET effctivity and the long-lived CS state (16 $\mu$s and 0.34 s, respectively) were evaluated [25].

Also corrole and corrole-fullerene were the subjects of investigations as future solar cell sensitizers [53,91–100]. In any molecular system, in which ET occurs it is necessary to conduct the research in thin layers with the use of polarized light to receive information about system ordering. The knowledge of the molecular system arrangement is extremely important because molecular organisation determines essentially EnT and ET processes [101]. L-B films have been successfully used for this purpose. Thus, spectroscopic behavior examined with the use of polarized light was widely studied for many different organic dye systems [68,87,91,96,97]. However, there are only a few papers that include studies of corrole and corrole-fullerene dyads nanolayers. The spectral studies of corroles and dyads in nanothin layers on quartz and gold plates were described for the first time in [91]. Two complementary experimental methods in the IR and UV-vis regions were used to evaluate orientation of the system on solid substrates. The models proposed by Arnold et al. [102] and Yoneyama et al. [103] are suitable for organic chromophores under supposition of the flat $\pi$-$\pi^*$ dye structure. The approach with the use of the infrared reflectance-absorption (IRRA) experiment [91] and Arnold model [102] provided the knowledge on orientation of the vibration transition moments of the bonds under assumption of its proximity to the corrole ring plane.

Fig. 8 shows the IRRA experiment in polarized light and in KBr pellet. The experiment done in the electronic region gave information on the electron transient moment and let to establish the corrole ring orientation of about $44^0$ in the presence of C60. The angle rises and it is about $46^0$ indicating charges redistribution and changing corrole ring orientation due to interaction of the corrole with the C60 [91]. This proposal was affirmed by the UV-vis results (Yoneyama model) which let to determine the orientation in the Soret ($39^0$) and Q regions ($34^0$) [91]. These results showed that orientation of the electronic and vibrational transition moments do not lie in the same plane. Also the important information received from IRRA is that the corrole and its dyad with fullerene is deposited on the Au substrate, and corrole is linked to the Au substrate *via* the carbon-fluorine group [91].

The examples of studies done for corrole photoactivity in a solar cell can be found in the papers of Salvatori et al. and Lai et al. [104,105]. However, the results presented in [104,105] did not show spectacular photovoltaic effectivity of the corroles under investigations. In [105] the results concerned the unsubstituted free-based 5–10-15 triphenyl corrole and its copper derivatives in a $TiO_2$-based solar cell; the values of estimated photovoltaic efficiency did not exceeded 0.02%. The result was interpreted as a weak charge injection associated with privileged charge recombination. The studies of Au-corroles linked to C70 were performed and described in [105]; the higher power photocurrent generation was observed and the value reached efficiency of about 6%. The list of photovoltaic parameters of vacuum-deposited solar cells based on organic compounds and C70 or C60 can be found in Lai et al. paper [105]. As expected, it was clear that the efficiency of current generation depends not only on the molecular structure of chromophores but also on a type of solar cells as it was shown in [104,105,106].

## Summarizing

In this paper it was underlined that the very advantageous approach in understanding and designing molecular photovoltaics is to follow and imitate some processes of the natural photosynthesis. In many papers photosynthesis was shown to be the process of a great wisdom. The $\pi$-electron dye-fullerene complexes perform EnT, ET and CS and thus they can mimic the primary processes occurring in the photosynthetic units. Thus, the extremely interesting and very important is to receive information on the principles that govern the relevant relationship between processes, properties, function and structure of photosynthetic pigments and molecular materials for photovoltaics. As said in Introduction photosynthesis presents the evidence of the most efficient natural device in which the EnT and ET as well as CS processes occur. Thus, it is essential to follow photosynthetic processes and to search for the photoactive materials that are able to convert solar energy into electric energy. One of them are corrole dyes. As discussed in this review corroles are suitable for this purpose.

Thus, the affirmative answer to the Graja's question referred to the title of his paper *Corrole-fullerene dyads: Will they replace corrole-fullerene systems?* given by him is *Yes*. In many papers one can find the arguments that support the use of corroles in solar cells: (i) corroles possess strong absorption in the Soret and red light regions and show clearly a quite broad energy region that covers sufficiently solar radiation, (ii) they have higher fluorescence quantum yield, (iii) they are characterized by the larger Stokes shift, (iv) they are characterized by lower first oxidation potentials, (v) they are easier to oxidize and more difficult to reduce, (vi) they are characterized by different coordination chemistry.

However, the question C*orrole and corrole-carbon materials* is still open and it needs much more investigations in the nearest future. It seems that more elaborate corrole-fullerene systems will be the next step for obtaining high quantum yield of charge separation and its long lifetime state and improve the cell architecture to design efficient devices for harvesting energy from sunlight and light conversion to electric energy.

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