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Interface Recombination & Emission Applied to Explain Photosynthetic Mechanisms for (e–, h+) Charges' Separation

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ABSTRACT

To copy natural photosynthesis process we need to understand and explain the physics underneath its first step mechanism, which is "how to separate electrical charges under attraction". But this Nature's nanotechnological creation is not yet available to the scientific community. We present a new interpretation for the artificial and natural photosynthetic mechanism, concerning the electrical charges separation and the spent energy to promote the process. Interface (e–, h+) recombination and emission is applied to explain the photosynthetic mechanisms. This interpretation is based on energy bands relative position, the staggered one, which under illumination promotes (e–, h+) charges separation through the action of an interface electric field and energy consumption at the interface of both A/B generic materials. Energy band bending is responsible by the interface electric field (and the driving force) for the charges separation. This electric field can be as high or above that for p-n semiconductor junctions (10^4 - 10^5 V/cm). This physical effect is not considered by most of the researches. Without an electric field and without spending energy to separate electrical charges, any other existing model violates physical laws. The staggered energy band type is the only energetic configuration that permits charges separation under illumination and energy loss to perform the process. Application to natural photosynthesis and artificial photovoltaic material and their energetic configurations are discussed. Examples for A/B being III-V/III-V, TiO_2/materials and II-VI/II-VI staggered energy band gap pairs are presented. In the proposed quantum mechanism, plants are able to eliminate most of the 79% of the absorbed visible light, according to the published reflection and transmission data. Moreover, the proposed mechanism can be applied to explain green fluorescent protein—GFP, charge transfer states—CTS and Fluorescent Resonance Energy Transfer—FRET. As recent literature experimental results propose photosynthesis as a quantum controlled mechanism, our proposition goes forward this direction.

Keywords: Solar Energy; Renewable Energy; Photovoltaic; Photosynthesis; Type II Interfaces; Staggered Interface; Interface Emission; Interface Recombination; Quantum Photosynthesis; Solar Cell; FRET; GFP

1. Introduction

Synthesis using light is the literal meaning of photosynthesis. It is the process by which plants are able to collect electromagnetic energy, mostly solar energy, that is used by organisms to synthesize complex carbon compounds. More specifically, light energy drives the synthesis of carbohydrates, which are essential for life. Thus, life on Earth ultimately depends on energy derived from the sun. Moreover, renewable energy is one of the most important scientific and technological topics on the current days, and a large fraction of the planet's energy resources results from photosynthetic activities in either present or ancient times (fossil fuels).

Photosynthesis first step, which is light absorption and separation of charges undergoing attractive electrical forces, is the most important physical/biological mechanism and should be copied in artificial systems such as solar cells. Therefore, photosynthesis must be understood at level of first principles, and based on physical parameters since photosynthesis is nothing more than a complex physical process [1-3].

Life started on Earth 2 - 4 billions of years ago, when the first two or more molecules got together, probably in a puddle of water, absorbing light from the sun and sepa-

rating both charges (e–, h+), perhaps catalysed by other factor as discharge and/or with the mineral environment participation. Since its first occurrence, this mechanism and the evolution of species on Earth gave us only one catalytic mechanism to separate oxygen from water [1]. The oxygen separation is one of the subsequent steps after the charges separation on photosynthesis' processes.

In the early days of Earth's exuberant vegetation, most of the available atmosphere gases were CO_2 and N_2. O_2 had appeared with the evolution of the charges separation process. Nowadays we have increased the CO_2 level from 200 (~1850) to 370 ppm (~2010) [1-3]. It has been an important point for scientists looking for renewable energy sources, and one of the issues is to copy the natural photosynthesis approach, related to the (e–, h+) electrical charges separation mechanism. The absorption of light by organic molecules or inorganic nanomaterials doesn't provide the electrical charges separation directly. This is just the first part of the process. If the material absorbs light, the following step is its recombination within the same material, releasing energy related the material's band gap energy (the forbidden band). To have (e–, h+) charges separation requires a suitable energetic configuration of the band gaps to allow the generation of the necessary electric field to separate the (e–, h+) pair. This electric field should arise from a potential variation. The mechanism that separates electrical charges of different polarities will be interpreted and described here. The expression "separation of charges of different polarities" means the separation of negatives, e–, from positives, h+, electrical charges, which undergo an electrical attraction called excitonic attraction. An appropriate electric field is necessary to break the excitonic attraction, *i.e.* to split both (e–, h+) charges, and hence energy must be spent. Any model that do not account for the electric field and the spent energy are violating physical laws. Our proposed model accounts for both: the necessary electric field and the spent energy. Furthermore, it seems to be the only energetic configuration capable of providing charges separation under excitation of light, and it is based on staggered energy band gaps between two different materials of nanometric dimensions.

At the interface, A/B, between generic materials A and B, there are naturally three possible energetic configurations of the band gaps: type I, type II and type III [4-12]. Type I interface are largely applied to construct solid state LEDs, laser, and most of the optoelectronics devices [10]. Type I energetic interface can be represented whenever the energy band gap of one material is inserted within the band gap of the adjacent material. Type III energetic interface occurs when the band gaps do not overlap [4-8,10]. Only the type II interface, the staggered one, shown in **Figure 1** will be discussed here, concerning its excitation by light and the bending of its valence and

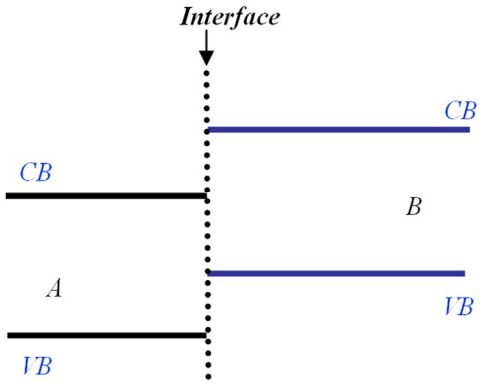

Figure 1. Flat band configuration for A and B materials staggered generic interface, representing the conduction band (CB or LUMO) and valence band (VB or HOMO). Note electrical charges (e–, h+) have always energetic steps (electric potential barriers up or down) when travelling from A to B or from B to A. This energy flat band configuration is a non-excited system; otherwise it should be band bended.

conduction energy bands. The band bending effect is caused by charges falling down to lower levels of energy states, creating a dynamic electric field that allows both (e–, h+) charges separation [4,10,12].

This paper is organized as follows. An introduction to type II interface and examples of applications on AlInAs/InP semiconductor system and other systems such as TiO_2/II-VI and II-VI/II-VI, emphasizing their very efficient mechanism for photon emission due to recombination of e– and h+ charges seated on different materials. Intriguing results on reflection and transmission, available on specialized literature for plants, will be discussed, for the first time, under the scope of physical principles. These discussions concern transmission and reflection experiments that give about 79% of absorption for natural leaves at the visible spectral region. Such very high photon absorption should "fries" leaves in few minutes in the absence of a fast optical emission mechanism to throw away much of the absorbed energy. We propose here that natural photosynthesis and artificial photovoltaics (nanometric systems) should be regarded as a quantum-controlled mechanism, differently of the currently accepted model, based on classical physics [1-10,13]. The present proposal provides both: the necessary electric field and the spent energy to separate negative from positive charges. It will be applied and discussed for both inorganic and organic systems. As explained below, the energetic relative position between two different materials is not a controversial question because modern organics LEDs and organic solar cells devices uses this concept. Moreover, many experimental results on energetic relative position and energy band bending on organics do exist, excluding the frequent "controversial" argument to avoid new ideas and explanation of the physical phenomena.

2. Current Representation of Energy Band Offsets between Natural Organic Materials

Photosynthetic' natural light reactions are represented by energy bands of different molecules that absorb light and transfer its energy to others molecules. This energetic representation is called "ground state energy" (GSE) [13-15]. According to Bjorn *et al*., the energetic relative position for molecules on leaves is unknown [15]. If it is unknown, experimental data should be performed to know their offset to get to actual scientific systems. The distribution of charges on excited organic molecules is somewhat different from the distribution represented on the GSE model. Unfortunately the GSE model, or representation, does not apply to any actual physical configuration; it leaves no room for feasible charge separation mechanisms in natural photosynthetic process. Existing electrical charges travelling from one to another different material have always energetic steps (up or down). The GSE energetic representation can not promote charges separation since there is no driving force to break the excitonic attraction [4,7,12]. Without the driving force, the GSE model and energy transfer mechanism model fails (see the discussion below, about fluorescence resonance energy transfer—FRET and green fluorescent protein—GFP). According to current believes, leaves are green to human eye due to chlorophyll molecules that absorb light mainly in the red and blue ranges of the visible spectrum; hence only light enriched in green wavelengths (about 535 - 550 nm) is reflected from leaves to our eyes [2]. However, there is no direct proof that the green colour of leaves is mostly due to reflection. In addition, there is no physical reason to explain why the leaves' colours are not related to emission. Note that leaves are de-pigmented (*i.e*., absence of green colour) when light is turned off. Equally, as presented below, excitation of leaves with green or higher energy photons gives many other colours' emissions. As it will be commented bellow, organic solar cells and organic LEDs, composed of nanometer thin layers, uses the concept and experimental results of staggered energy band gap configuration, in contrast to the GSE configuration. As GSE is not feasible in physical systems, the staggered band energy configuration (**Figure 1**) provides the major benefit for the light reaction of photosynthesis: the electric field (driving force) for (e–, h+) electrical charges separation. At the interface, the electric field comes from the nearby A/B materials interface energy band bending (**Figure 2**), and the interface light emission can be related to the spent energy, associated to the charges separation.

In conclusion for this section, organic molecules present on leaves should experiment energetic (or potential) steps for electrical charges movements between them. Without these energetic steps it is impossible to propose a mechanism for charges separation for the natural and artificial photosynthetic processes. By using non-existing physical energetic configuration (e.g., the GSE configuration) we fail in explaining the physical mechanisms. Any model based on non-existing energetic configuration bring us to violate physical laws whenever trying to explain the physical mechanisms. The light absorption by molecules within leaves is only the first step of the process and it does not separate e– from h+. The next step, to separate e– from h+, depends on the energetic configuretion between the existing molecules within the leaves. Type II (staggered) energetic interface is proposed to overcome the problem.

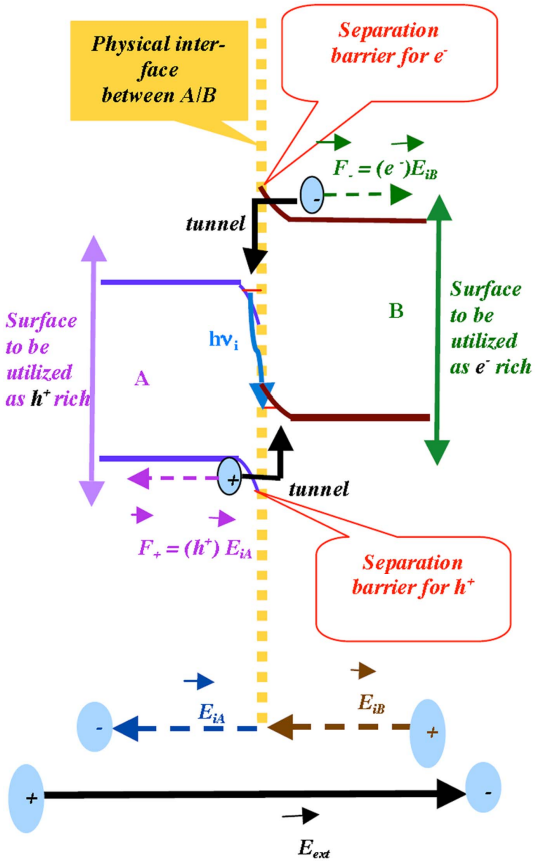

Figure 2. Type II interface representation under light excitation of both A and B materials and the interface energy band bending on both sides. These energy band bending are created by the e– and h+ charges falling down to the lower energetic steps at the interface (including possible tunnelling of charges). The interface energy band bending creates electric fields on both sides, responsible for the charge separation to the opposite interface's directions (the driving force F_- & F_+). $h\nu_i$ represents the interface photons energy emission, related to the spent energy to separate (e–, h+) charges under excitonic attraction. The interface energy band bending (or the electric potential) gives rise to the electric field E_{iA} & E_{iB}. Note that the $h\nu_i$ interface emission is also issued from a tunnelling mechanism. E_{ext} is the external electric field applied to the AlInAs/InP structure, as explained in the text, to decrease the $h\nu_i$ emission intensity.

3. Current Energy Band Offsets Representation between Inorganic Materials

The artificial photosynthetic mechanism (applied to modern solar cells) is currently and conveniently represented by type II interfaces (the staggered one, represented in **Figure 1**) [16-21]. But the model frequently fails because the semiconductors interface band bending phenomena is not considered, whenever charges fall down to lower energy levels at the interface between two A/B generic materials [4-7,10,16-21]. Only the flat band configuration is considered for most of the artificial photosynthetic process. With no energy band bending considerations, there is no electric field (driving force) to separate both charges of different signals, as represented in **Figure 2**. The staggered energetic representation for artificial photosynthesis does not consider that the falling down of electrical charges at the interface is a sink for them [16-29]. Once these charges cross the interface, they recombine there and they are lost because the recombinetion gives rise to interface emission [7,9,23-29]. This interface recombination is erroneously and frequently called charge transfer state (CTS) [27-29]. The authors do not understand why the expression "charge transfer state" is applied, since it is simply interface recombination and emission. These CTS are applied to organic and inorganic systems and it will be discussed below in more details.

Note that both natural and artificial photovoltaic mechanisms described above are dynamic systems, as represented in **Figure 2**. It is the near interface electric field; created by the electrical charges falling down, that separates e– from h+ [4-7]. This interface electric field arises from a varying potential (or energy band bending). Without illumination the flat band condition takes place, as presented on **Figure 1**. As soon as (e–, h+) pairs are no longer created (no excitation), there are no longer electrical charges falling down to lower energy steps at the interface. Without light, the equilibrium condition is achieved and there is no more interface energy band bending (no electric field, able to separate e– from h+, as presented in **Figure 2**). At this moment, the interface light emission stops. Note that the consumption of (e–, h+) pairs at the interface (by interface emission) brings the A/B system to equilibrium, without external excitation. As the present proposal represents a different regard on photosynthetic systems, it will be described below step by step, bringing the necessary physical tools and experimental proofs of its existence.

In conclusion for this section, inorganic photovoltaic nanomaterials present the actual band offset (the staggered one), but suffers from the mains physical tools to separate electrons from holes: the necessary electric field and the spent energy to separate electrical charges under attraction. The physical laws' violation is twofold in this case, even though the experimental results are very important for solar energy developments. The physical mechanism to separate (e–, h+) is not present.

4. Physical Principle of the Charge Separation Mechanism

According to the Nobel Prize Laureates L. Esaki (1973) and H. Kroemer (2000), the staggered energetic configuration between two different A/B materials, the flat band configuration (no excitation), is presented in **Figure 1**. This representation is only for the conduction band (CB or LUMO) minima and valence band (VB or HOMO) maxima at the momentum configuration (K space) [4-7, 10]. These minima and maxima are related to parabolic energetic representation of energy on K space [10]. Under A and B light excitation, it takes the configuration showed in **Figure 2** where we can observe: (e–, h+) pairs generation; e– and h+ jumping to lower energetic steps at the interface and, consequently, the energy band bending of both bands CB and VB in both A and B materials. Such jumping of charges leaves both materials into a non-equilibrium electronic state. Note that the jumping of charges to the nearby material put both A and B materials under non-equilibrium electronic condition [4,8,10]. This non-equilibrium electronic condition should move both quasi-Fermi energy levels on both sides of the interface. Moving both quasi-Fermi energy levels, should move (bend) both CB and VB on both sides of the interface [4,7,10]. The interface energy band bending creates barriers for few remaining electrons and holes (at the CB and VB of both materials). These few remaining charges are no longer allowed to go across the bended barriers. Their thermal energy is not enough to promote tunneling across these barriers. The electrical charges are therefore sent away from the interface by the gradient of the electric potential (the electric field being $\mathbf{E} = -\mathbf{grad}\ V$). They represent the separated charges by the energy band bending action (and by the interface created electric field on both sides of the interface) [4,10]. The (e–, h+) that fall down to the lower interface energy steps recombine at the interface, giving rise to the interface recombination and photons emission ($h\nu_i$). These emitted photons are lost, representing a faster and easier way to efficiently waste photon energy for A/B generic systems. Interface energy band bending is frequently used as a result of charges falling down to lower available energy levels [4, 7,10]. As the interface electric field ($\mathbf{E}_{iA}$, $\mathbf{E}_{iB}$, **Figure 2**) comes from the potential variation at both sides of the interface, we have the necessary electric field and the driving force to separate electrons from holes. Note that potential variation and energy band bending are related, since energy = potential × electrical charge. Shortly, most of the excited charges jump, creating the band bending, and few excited charges do not achieve to cross the barriers

created by those crossing the interface. A support information file represents the proposed mechanism, for a generic A/B interface, excited with only four photons, in a slow motion representation way [SI-1].

The interface energy band bending is not frequently considered on photovoltaic artificial experiments and conclusions [16-21,27-29]. Without the energy band bending there is no interface electric field. Without an interface electric field (both, $\mathbf{E_{iA}}$ and $\mathbf{E_{iB}}$, in **Figure 2**), (e–, h+) charges do not get separated. Note that energy band bending and Fermi level movement follow each other [10]. On nanostructured materials their size is too small to consider diffusion controlled mechanism [10, 16-22]. Carriers' diffusion length on bulk materials is many orders of magnitude of that of the size encountered on nanosized materials [10,22]. In this way the charges separation explanation and the charges displacement direction are not physically correct in many published papers [16-21,27-29]. On the other hand, the dynamical bending of the energy bands (and Fermi level), as proposed here, is perfectly in agreement with all physical concepts, providing the fundamental theoretical explanation on how charges get separated on such systems, as detailed below for TiO_2/II-VI and II-VI/II-VI semiconductors systems [4,10].

To each (e–, h+) recombination at the interface, a photon of energy $h\nu_i$,

$$h\nu_i = \Delta S + \Delta Q_e + \Delta Q_h - \Delta E_x \qquad (1)$$

is emitted (**Figures 2** and **3**). ΔS is the overlap of the energy bands of the A and B materials without excitation, *i.e.* in the flat band configuration (**Figure 3**); ΔQ_e is the electron energy quantization within the interface quasi-triangular shape quantum well; ΔQ_h is the hole energy quantization within the interface quasi-triangular shape quantum well and ΔE_x is the electron-hole excitonic interaction energy. Note that $h\nu_i$, the interface energy emission, is always lower than both A and B band gap materials. So, material B band gap energy > $\mathbf{h\nu_i}$ < material A band gap energy. This can explain many lower energy peaks on composed type II interfaces presented in the literature, but not understood up to now [16-29]. As already mentioned, this interface photons emission is erroneously called charge transfer state [27-29]. But it is just an interface (e–, h+) recombination and emission. This energy is lost but it is at the origin of the band bending and interface electric field.

Figure 3 represents the energy balance at the A/B system when excited by photons with enough energy to promote electrons from the VB to the CB on both A and B materials. By exciting the A and B materials, the falling down of electrons from B to A increases the interface electron density, represented by ΔQ_e (negative electrical charges on A). In the same way, the falling down of

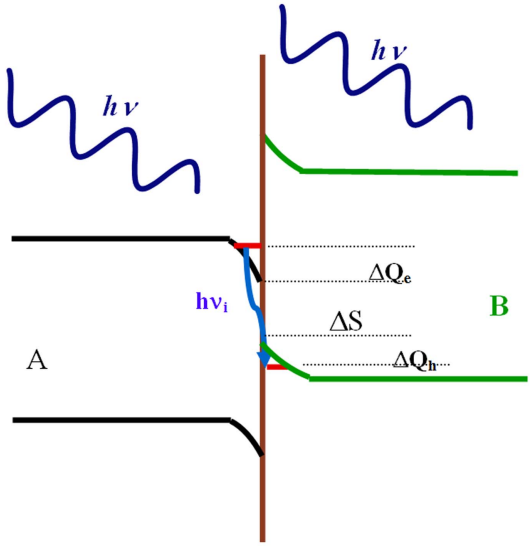

Figure 3. Energy balance at the A/B interface. The observed interface photon emission is represented by $h\nu_i$, which depends on ΔS, the non excited A/B energy band gap overlap, the ΔQ_e, electron quantized well energy, the ΔQ_h, holes quantized well energy and the ΔE_{ex}, electron-hole excitonic energy. Note the interface energy band bending depends equally on the $h\nu_i$ the photon external excitation energy. Equally, ΔQ_e & ΔQ_h depend on $h\nu_i$.

holes from A to B increases the interface holes density, represented by ΔQ_h (positives electrical charges on B). As a consequence of a high density of opposite sign electrical charges at the interface, a high ΔQ_e and ΔQ_h interaction appears. Note that both quasi-Fermi level should follows these charges movements [10]. This high (e–, h+) interaction at the interface, represented by ΔE_x, the excitonic interaction between e– and h+, ΔE_x, is of the order of few to tens of meV for bulk semiconductor materials. ΔE_x is of the order of hundreds of meV for organic molecules [10,22]. This ΔE_x physical energy parameter for (e–, h+) interaction (but seated on different materials) generates a strong interface emission (electrical charges wave function barrier penetration or tunneling). It is important to register that the ΔE_x value have never been presented in the literature for (e–, h+) pairs seated on different materials, for type II (staggered) interfaces recombination and emission, represented by $h\nu_i$ [10,22].

Note that the falling down of e– and h+ to the nearby material should move quasi-Fermi level meanwhile band bending takes place. Electrons leaving material B (**Figures 2** and **3**), the quasi-Fermi level should go down on material B. Holes leaving material A, the quasi-Fermi level should go up on material A [10]. Both ΔQ_e and ΔQ_h create an interface electric field from the material B to the material A. It has the same direction of both $\mathbf{E_{iA}}$ and $\mathbf{E_{iB}}$ on **Figure 2**. Note also that the Fermi level (no excitation, **Figure 1**) depends on the materials doping conditions

and the quasi-Fermi levels depends on doping and external excitation (**Figures 2** and **3**) [10]. This question will be discussed below for the AlInAs/InP system and presented at the support information 1 [SI-1].

Figure 4 represents an A/B interface composed by a staggered excited system, with both exponential (quasi-triangular) shape quantum wells for electrons (material A) and holes (material B). The wave functions probabilities for the (e–, h+) pairs are equally represented. Calculus (Support Information 2 [SI-2]) were performed for the InP/AlInAs system and based on physical parameters available in the literature [23]. Details of the calculus for the (e–, h+) wave functions overlap, energy band bending and existing electric field at the InP/AlInAs interface is presented elsewhere [23, 30 and in SI-2]. In this work (**Figure 4**) the energy bands are modelled as exponential bended bands, leading to Bessel wave function for carriers. Energy levels of carriers at valence and conduction bands, as well as the penetration depth, for each kind of carrier are obtained by solving the transcendental equation obtained for wave function continuity at the interface. Note in **Figure 4**: electrons have one and holes have two wave functions probabilities representation. The wave function probabilities with about 2 nm and 1 nm of barrier penetration, respectively for e– & h+, are represented in this **Figure 4**. Both barriers wave function penetration are enough to explain the strong interface photons emission discussed below and presented on **Figure 5**. The barriers wave function penetration and the strong interface emission observed by the authors and many others research groups corroborate our comments on type II interface physical parameters [12,19,23-25, 27-29]. Note that this interface quantum controlled mechanism (wave function penetration, tunnelling) is valid for II-VI and for III-V A/B generic materials' interfaces [16-21,23-25,27-29].

Interface recombination is a dynamical quantum process and a very efficient emission mechanism. As the light excitation intensity upon the system increases, the electron cascade from upper to lower CBs energy levels, enhancing the band bending effect. So, the interface emission is liked and responsible for the CB and VB energy band bending and it is also associated to the spent energy for the charges separation, represented in **Figure 2**. The falling down of electrical charges at the staggered interface creates the band bending on both sides of the A/B system (Support Information 1 [SI-1]). The charges falling down increase ΔQ_e and ΔQ_h values and the interface emission. As a consequence there is also an increase at the quasi-triangular shape well deepness (represented by the energy band bending in **Figures 2** and **4**) at the same time. By increasing the well deepness, it increases the interface PL intensity and broadens the interface peak emission, $h\nu_i$. It also increases the (e–, h+) wave function barrier's penetration and tunneling. The intensity and broadness of the interface emission, as discussed below, occurs due to the lack of QM selection rules. The interface light emission is a very efficient (e–, h+) recombination mechanism [23-25,27-29]. Note that the effect is double on each side in both sides (leaving e– and receiving h+), increasing band bending (or increasing the interface electric field $\mathbf{E_{iA}}$ & $\mathbf{E_{iB}}$). The low efficiency of the presented model for charges separation mechanism corroborates and can explains the low efficiency of natural and artificial systems (1% - 6%). This is the reason for most of the photons energy loss at the interface and the movement

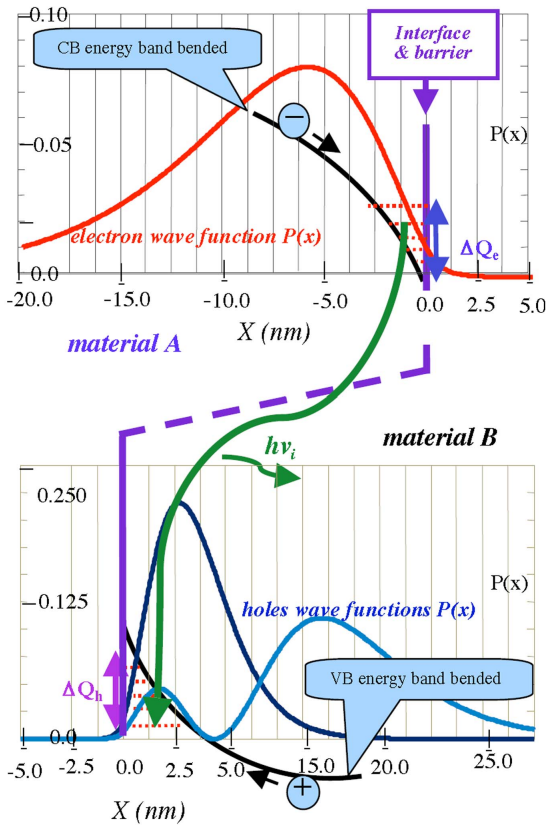

Figure 4. A/B material excited interface, presenting the CB band energy bending for electrons and its quantum well energy levels, and the VB band energy bending for holes and its quantum well energy levels. X represents the distance from the interface in nanometer (nm); $h\nu_i$, the photon interface emission following the (e–, h+) interface recombination; and P(x), the (e–, h+) wave function probability to be found on A or B. Note there are two holes wave function probability for the conditions we use for the simplified calculations [30 and SI-3]. As the energy band bending depends on the photon energy excitation, many energy levels are expected on these wells, owing to the spectral FWHM width presented in Figure 5 (34 to 36 meV at 77K). The P(x) value penetration for holes on A is about 1 nm; for electrons on B it is about 2 nm. These values are enough to account for the interface intense emission PL peaks observed in Figure 5 (1.303 and 1.193 eV). Similar results are presented on references [23-25,27-29].

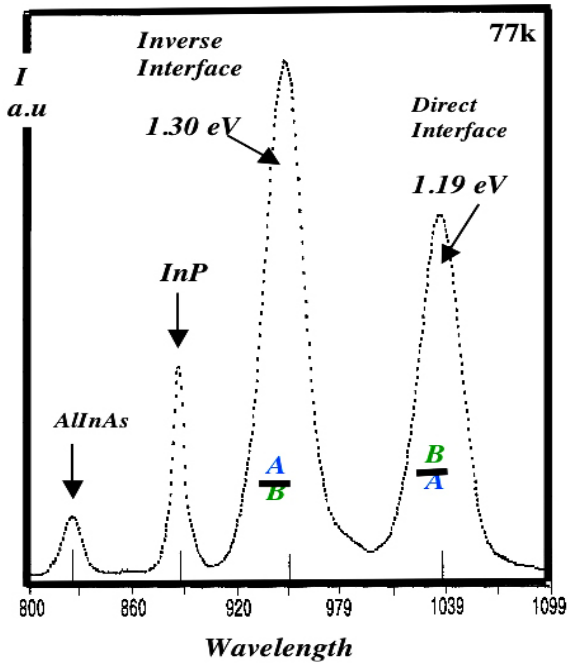

Figure 5. 77 k photoluminescence (PL) intensity (I) versus wavelength experimental results of an InP/AlInAs/InP (A/B/A) energy staggered interface. Both interface emissions (1.303 and 1.193 eV) are very intense and broad, compared to the bulk InP (1.395 eV) and bulk AlInAs (1.499 eV) emissions. These InP and AlInAs PL emissions are observed due to the ternary layer thickness (1.6 µm), above the carriers mean free path diffusion length (allowing AlInAs CB-VB transitions and observation) and the binary layer thickness top layer (0.1 µm, allowing InP CB-VB transitions and observation) [9,23,24]. Both materials are intrinsically n-type doped (AlInAs ~10^{16} at/cm^3, InP ~10^{15} at/cm^3).

of few e– and h+ away from the interface (in opposite directions). Moreover, it is a quantum-controlled system as it will be exemplified below, for inorganic/inorganic A/B systems, and as proposed for the photosynthesis modern experiments.

In conclusion for this section, the necessary physical tools to separate e– from h+ and recombination at a type II interface energetic configuration is presented. It is based on an existing energetic configuration, already described for inorganic materials. Whenever electrons jump from material B to material A (**Figures 1-3**), they leave material B under excess of holes and under electronic non-equilibrium condition. This non-equilibrium condition moves the quasi-Fermi level down and conduction band moves up on material B. Whenever holes jump from a material A to a material B, they leave material A under excess of electrons and under electronic non-equilibrium condition. This non-equilibrium condition moves the quasi-Fermi level up and the valence band down on material A. Most of the excited A/B interface charges recombine when jumping, but this event has created a gradient in the electric potential and an interface electric field. As the jumped charges are lost and emitted as $h\nu_i$, their act promotes the necessary condition to separate few non-jumped electrical charges. In this case we have both physical tools to separate e– from h+: the electric field and the spent energy, without violating physical laws.

5. Application to the InP/AlInAs/InP Staggered System

The III-V semiconductors can be easily grown through the metal-organic chemical vapour phase (MOCVD) technique [9,23-25]. The InP/AlInAs system has a staggered energy band gap relative position [7,9,23-25]. As a staggered A/B system, it presents an interface $h\nu_i$ strong emission. The A and/or B band gap emission observation (bulk material) depends on the layers thicknesses, whenever A/B interface is grown. For an InP/AlInAs thin film thicknesses (below carriers diffusion length << 1 µm), the optical response presents only the interface emission, which energy is about 1.193 eV [9,23,24]. For thicker films (above carriers diffusion length, ≥ 1 µm), the interface emission is still the predominant optical phenomena. **Figure 5** presents the photoluminescence of an InP/AlInAs/InP system, where two staggered interfaces are present. The one called direct: AlInAs grown on InP (with a 1.193 eV emission peak) and the one called inverse interface (InP grown on AlInAs, 1.6 µm thick, with a 1.303 eV emission peak) [9,24]. Both interface peaks' emission are broad (34 - 36 meV at 77 k and 70 - 80 meV at 300 K) and intense, characteristics of type II interface emission. These broad energy peaks are related to the ΔQ_e and ΔQ_h available energetic states presented in **Figures 3** and **4** and Equation (1). As (e–, h+) are located in different materials, the recombination occurring at the interface takes place free of any quantum mechanical **k** selection rule (**k** = momentum), following the lack of lattice periodicity (e– and h+ are seated on different materials). This fact improves the probability of recombination, making it a more efficient mechanism, as observed in **Figure 5**.

As the MOCVD growth conditions does not allow ease change from As to P chemical elements, the InP growth on AlInAs possess a much wider transition interface and, consequently, the bands offsets are not the same as for AlInAs grown on InP. The inverse interface has an InAsP (about 6 nm) transition layer, as stated by Auger spectroscopy [9]. These results proof, even with non-optimised (non-abrupt) staggered interface, the interface recombination mechanism is still predominant for 0.1 to 1.6 µm tick AlInAs layers [9,23-25]. For nano-sized materials these effects should be much more pronounced, as it occurs with TiO_2/II-VI semiconductors materials applied to solar cells research [26-29]. The laser excited AlInAs/InP direct interface fluorescence, with 1.193 eV energy peak emission, shown in **Figure 5**, creates the

energy band bending on both sides of the interface. These energy band bending (or varying electric potential) can be evaluated by solving Poisson's equation on both sides of the interface (see support information 3 [SI-3]). A simple estimation (not shown) for the (e–, h+) dynamic electric field is from 0.4 × 10^5 V/cm ($\mathbf{E_{iB}}$, material B = AlInAs) and 1.24 × 10^5 V/cm ($\mathbf{E_{iA}}$, material A = InP) [25,30,31,SI-3].

To decrease the interface PL (measured at 12 to 77 K) 1.193 eV intensity to zero, an external electric field of about 10^5 V/cm should be necessary, represented in **Figure 6** [25,31]. This is the physical condition to cut off (stop interface emission) the charge falling down to lower energy steps of the present AlInAs/InP structure. Surprisingly this is approximately the electric field necessary to decrease to zero the interface emission intensity of a similar AlInAs/InP structure published by Sakamoto *et al.* ([25], its **Figure 1**, PL intensity extrapolated to zero, plotted as a function of the external applied electric field, which value is 0.55 × 10^5 V/cm) [31]. Our PL experiments shown in **Figures 5** and **6** are in accordance with the results of Sakamoto and co-workers and reveal how important is the existing high value electric field at the excited type II interface [9,23-25,31]. Note that this electric field is comparable to the p-n Silicon semiconductor junction electric field (10^4 to 10^5 V/cm) [10]. Attention should be taken because it is compared to the extrapolated 12 K and 77 K electric field values [25,31]. The error percentage is low between 12 K and 77 K [10]. Comparing the estimated electric field (caused by band bending at the AlInAs/InP interface, 77 K) with that of a Silicon p-n junction (about 10^4 - 10^5 V/cm, at 300 K) it gives an idea about the dimension of the excited type-II interface electric field, as exposed in **Figure 6** [10,30,31]. This comparison is proposed only to give the order of magnitude of the AlInAs/InP excited interface electric field. Moreover, the order of magnitude of a light excited AlInAs/InP type II interface electric field is known for the first time [10,25,31]. Note that **Figure 6** presents results of the clear proof of the interface electric field at a type II, staggered excited interface. These $\mathbf{E_{iA}}$ and $\mathbf{E_{iB}}$ (**Figure 2**) interface electric fields, added because they are in the same direction, issued from CB and VB band bending (due to the jumping of e– and h+ at the interface) are responsible by the few others e–, h+ running to the opposite side of the interface. They are the separated charges by type II interface (the driving force, $\mathbf{F_-}$ & $\mathbf{F_+}$ represented in **Figure 2**).

As it will be mentioned below, to the staggered model, applied to organic molecules (chlorophyll in leaves, for the photosynthesis mechanism), the interface dynamic electric field should be much more pronounced because of the nanometer size dimension and distances within the Natural system in plants. Note that electric field depends

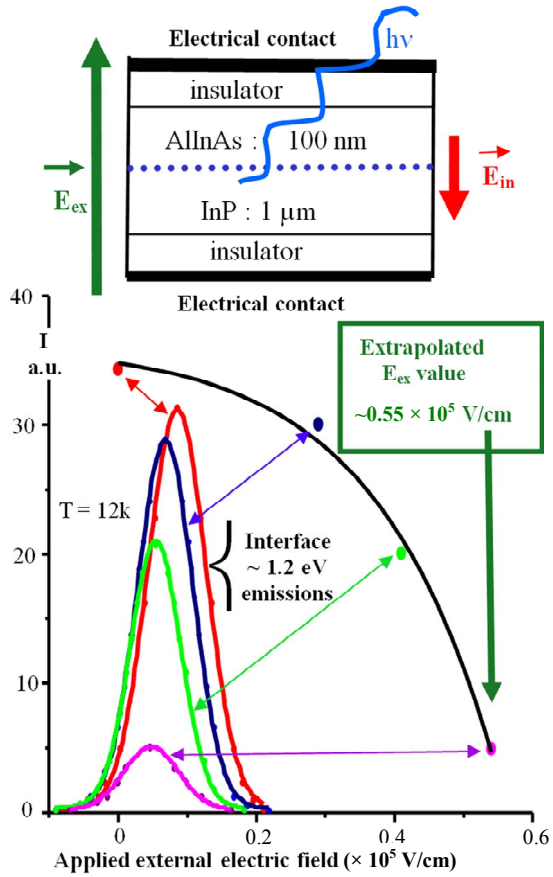

Figure 6. Top: explored structure. Botton: PL intensity (I) versus external applied field. Experimental results on type II interface emission (~1.2 eV, at 12 K) for an AlInAs thin layer (100 nm) grown on InP. The PL peaks were withdraw from [23-25]. Applying an external electric field to the structure (E_{ex}), the interface emission ($h\nu_i$) reaches zero intensity. For this structure, as the AlInAs thickness is below the charges diffusion length, we observe only the interface emission peak; InP and AlInAs peaks are very low intensity. This experiment shows that energy band bending gives rise to the interface electric field (E_{in}), able to separate e– from h+. Application of an external electric field (E_{ex}) to the AlInAs/InP structure, the 1.2 eV interface emission goes to zero with E_{ex} ~0.55 × 10^5 V/cm (E_{ex} cancel E_{in}) [25]. This is the clear proof of the interface electric field (E_{in}) related to the potential variation (band bending) and interface emission. Note that the 1.2 eV interface emission peak moves to lower energy as E_{ex} increases, as ΔQ_e and ΔQ_h decreases (Equation (1) and [25]).

inversely on the square of the distance between two electrical charges. These results are applied to organic systems, as already published, to produce type II energetic interfaces for LEDs and organic solar cells, discussed below. Fortunately, recent publication on organic LEDs and organic solar cells use experimental results of type II interface. Unfortunately energy band bending is not frequently applied to organic devices. In contrast, natural photosynthesis models fail on scientific physical basis

without the use of staggered configuration. It fails too for energy band bending for the charges separation mechanism, by using the flat band condition. The broadness of interface emission will be discussed below.

In conclusion for this section, we show an AlInAs/InP staggered inorganic system that, under optical excitation, creates an interface electric field that can be cancelled by an external electric field of about 10^5 V/cm. The interface emission presents a very intense and broad peak. The high intensity coming from the lack of quantum mechanical selection rules, as yet discussed above. The optically created interface electric fields ($\mathbf{E_{iA}} + \mathbf{E_{iB}}$) are responsible for the very inefficient charges separation mechanism on type II systems.

6. The Interface TiO_2/Material and II-VI/II-VI Staggered Systems

In this item we present some comments on published results on TiO_2/(B materials) and on (A:II-VI)/(B:II-VI) interfaces. We show why the published articles do not represent the real physical situation for charges separation, although the experimental results are very important. The lack of correct physical situation, mainly represented by the absence of an electric field to separate e– from h+, corroborates to the presentation of the electrical current across the system without a true scientific support.

TiO_2 is a semiconductor material which energy band gap ranges from 3.1 to 3.4 eV, depending on the physical phase and crystal quality. The TiO_2 anatase phase is one of the most applied to photovoltaic experiments [11, 16-21,32-34]. Recently a huge amount of experimental work has been performed on the TiO_2/II-VI system compounds [16-21,26,32,33]. Between these systems it can be found nanomaterials such as TiO_2/(CdTe, CdS, CdSe), TiO_2/metals, TiO_2/oxides, TiO_2/organics, CdSe/CdTe, etc [8,11,16-21,26-29,32-34]. Most of these recently published work on the nanosized systems of TiO_2/material and CdTe/CdSe use the flat band gap energy configuretion, presented on **Figure 1**, for nanomaterials photovoltaic experiments (under light excitation) [16-21,26-29, 32,33]. According to their represented flat band configuration, the photon excited electrons move from the material B to the material A (TiO_2) (**Figure 1**). In the same configuration of **Figure 1**, holes fall down from material A to B. Unfortunately, these electrical charges (e–, h+) movements do not describe the actual net charges movement to achieve the generated photocurrent [4-7,10,12, 16-21,26-29,32-34]. In addition, (e–, h+) fall down at the interface, energy band bending should be considered to give the real electrical charges movement direction: ordinary semiconductor physics theory and experiments are not considered by these authors [4,10]. The interface (e–, h+) falling down of carriers and their recombination at the interface are not considered [4,7,9,10,12,23-25]. These interface (e–, h+) recombination decreases photovoltaic efficiency and, mostly, it is not reported because it is not understood. In summary, are absent: the electric field, able to separate electrical charges and the spent energy to perform this process.

The II-VI/II-VI systems, presenting type II interface, have been applied to photovoltaics, as it occurs with CdTe/CdSe nanocrystals, in which an interface energy emission of 1.5 - 1.6 eV has been observed and erroneously attributed to "charges transfer states" on photovoltaic experiments [27,29]. These interface energy emissions are similar to the presented in **Figures 5** and **6** (1.2 - 1.3 eV). Unfortunately basic semiconductor physics has not been considered by these authors, as well as the energy band bending and the necessary electric field to separate electrical charges having different polarities [4-7,10, 23-25,27-29,32-34]. Moreover the interface energy emission is considered a "charge transfer PL peak" without explaining what does it means [27,28]. Indeed they consider that CdTe/CdSe experiences an energetic driving force for charge transfer, holes finding lower states in the CdTe and electrons occupying lying CdSe states [29]. And more, it is considered that carrier extraction is driven not by means of a built-in electric field from a depletion region due to substitutional dopants; rather extraction is primarily caused by direct diffusion as dictated by type II heterojunction [29]. These conclusions show clearly the misunderstanding of type II interfaces. Note that the 1.5 - 1.6 eV CdTe/CdSe interface peak is broad and symmetric [27,29]. The same characteristics are present on the AlInAs/InP, as presented in **Figures 5** and **6**.

Strictly speaking, photovoltaic TiO_2/materials and II-VI/II-VI electrical charges movement directions' interpretation is not correct for the recent nanomaterials experiments [16-21,27-29]. The same problem occurs with photovoltaic artificial nanostructured materials and should be interpreted as well as for leaves from plants [2,15, 16-21]. For plants, the staggered energy configuration is not considered. For the artificial TiO_2/materials or II-VI/II-VI systems the energy staggered configuration is considered, but not the energy band bending configuration for the excited system. Indeed, the molecules' energy interface band bending is neither considered for plants, representing a non-physically and a non-scientifically sustained condition. Moreover the dynamic electric field at the materials' interface (TiO_2/materials and natural systems) should jump from 10^4 - 10^5 V/cm for 1 μm length ordinary silicon p-n junctions to much higher values for the nanometer scale of inorganic (TiO_2/materials or II-VI/II-VI) and/or organic molecules inside a leaf [10,27-29,32-34].

This electric field value represents a huge change within the photosynthetic artificial and natural world, not considered up to now. As mentioned above, to cancel the

interface electric field of a light excited AlInAs/InP staggered system we need an external electric field about 0.55×10^5 V/cm [25,31]. These physical principles represent a just known simple semiconductor interface physics, not considered up to now [4-10,12,23-25,31].

In conclusion to this section, type II interface, applied for TiO_2/(B material) and A:II-VI/B:II-VI systems, uses the right energetic configuration but do not propose the necessary physical tools to separate electrical charges under attraction: the electric field (issued from the energy band bending) and the spent energy (issued from interface recombination). The flat band representation for excited systems does not hold on physical basis. Under photons excitation, the jumping of charges to the nearby material brings the near interface to a non-equilibrium condition on both A and B material's electronic structure and, consequently, it brings the energy band bending (or potential variation) and the Fermi level movement (dynamic process). The interface recombination is erroneously attributed to "charge transfer states" that is not understood by the authors of the present work. Charge transfer states are confused with interface recombination and emission, related to the spent energy (loss) to separate e– from h+.

7. Why Is the Interface Emission So Broad

In our model, the interface emission comes from two quasi-triangular quantum wells, representing energy states within ΔQ_e and ΔQ_h (Equation (1) and **Figure 7**). As the deepness of these quantum wells depends on the number of charges jumping to the nearby material and these numbers depends on the number of arriving photons, the emission peak ($h\nu_i$) will depend on both terms ΔQ_e & ΔQ_h. Moreover, without QM selection rules, charges on each energy level on ΔQ_e is supposed to recombine with charges on each energy level of ΔQ_h. It gives rise to the broad interface emission. Note that ΔE_x (excitonic attraction, Equation (1)) should also be dependent on the optical excitation intensity and on ΔQ_e and ΔQ_h.

As guidelines for type II interface properties, the main characteristics of type II interface can be summarized as follows:

1) It is a very efficient (e–, h+) recombination quantum mechanical mechanism (but with no QM selection rules). Note: e– mobility >> h+ mobility, able to allow an interface permanent e– population inversion;

2) It is a very intense and efficient photons interface's emission;

3) It has a very broad interface emission peak: $h\nu_i = \Delta S + \Delta Q_e + \Delta Q_h - \Delta E_x$ (these quantities are explained on **Figure 7**). Note that the peak broadness, FWHM α f (excitation intensity and excitation wave length);

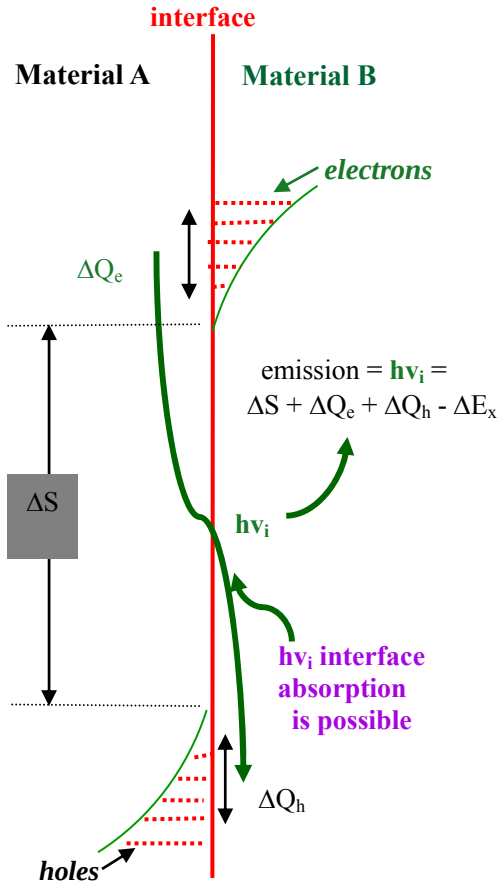

Figure 7. Representation of the main characteristics of type II interface emission: two quasi-triangular shape quantum wells (QW) are present on opposite side of the interface and the energy levels in these QW. The luminescent interface peak is large and intense due to: (a) (e– & h+) are localized on two different materials on quasi-triangular shape quantum wells, on both sides of the interface; (b) The deepness of both A/B materials' interface quantum wells, $\Delta Q_e + \Delta Q_h$, depends on the excitation density (number of arriving photons); (c) Absorption and emission by the interface are possible; (d) The excitonic interaction (ΔE_x) and the e– & h+ wave function overlap should also depend on the excitation density. Note that the lack of quantum mechanics selection rules for (e–, h+) recombination at the interface is a consequence for both (e–, h+) seated on different materials (no symmetry).

4) It is a symmetric emission peak (related to the density of states in two quasi-triangular quantum well). Note that pure CB to VB transitions show a non-symmetric PL peak due to the non-symmetric density of states on their respective bands [10,22];

5) It has an energy emission with a below both A & B materials band gap emissions (red shift);

6) It is related to the spent energy (waste) to create energy band bending at the A/B materials' interface;

7) It can be associated to FRET or GFP (proposed as an energy interface emission, instead) [SI-3];

8) It can be associated to the charges separation mechanism (electric field and spent energy to separate e– from h+);

9) Note that absorption/emission by a type II interface cannot be discarded. In this case, a VB excited electron can jumps directly from a material to the nearby material. In this case, excitation/emission can be at or near the same wavelength. A question mark comes about: could it be possible that specific molecules do not present absorption peaks caused by this effect (absorption and emission at the same wave length)?

10) It can be related to the low efficiency (1% to 6%), obtained for photovoltaics using type II interface systems. It is a very efficient way to waste photon energy at the interface (maybe ~70% of the absorbed photons on leaves for the visible spectral region).

In conclusion to this section, type II interface recombination/emission has not yet been correctly used to explain many physical aspect related to photovoltaic systems. The main properties: intensity, broadness and symmetry of its emission peak have not been considered by the majority of the artificial photovoltaic community. The broadness of the interface emission is due to the many energy levels (quantum confinement) on the CB, available to the many energy levels available at the VB, without rules for their recombination. The interface recombination remains a quantum mechanics mechanism even if the transition/recombination from e– and h+ located on different materials do not need to follow QM selection rules.

8. Energy Staggered Band Gap Configuration Proposed to the Photosynthesis First Step Mechanism (Charges Separation and Spent Energy)

As already described, the "ground state energy" configuration for two A/B materials does not represent any actual physical energetic configuration [13,15]. Nature has created energetic steps for charges travelling from one to another different material [4-11]. It represents general rules for A and B organic and/or inorganic materials. For molecules from plants (e.g., carotene, chlorophylls), A/B represent an organic/organic energetic interface. May be the staggered configuration on organics/organics materials interface is unknown for many researchers. Experimental results on energy band bending are now available [35,36 and references therein]. Organic molecules band bending has been mentioned in published articles and charge transfer modify the energy level alignment [35-38]. It cannot be considered as a controversial subject because it is based on experimental results. Moreover, when electrical charges jumps from a material to its neighbour, both electronic structures change, otherwise there is violation of physical laws. So when electrical charges move from a molecule to another, the energy band bending is unavoidable. This band bending represents the necessary electric field to separate electrical charges of different polarities. The interface jumped e– and h+ are under excitonic attraction and they can recombine emitting $h\nu_i$.

The amount of published articles on photosynthesis, considering the physically non-existing "ground state energy" (GSE) configuration is huge up to now [13,15]. Even for initially considered type II inorganic interface (CdTe/CdSe), the authors turn to the ground state energy to try to explain their results, which is an erroneous action, to explain the charges separation in their system, using GSE model [27-29]. This GSE energetic configuration suffers with two main drawbacks, bringing to an uncomfortable scientific situation about the non-existence of the energy band bending between two light excited A/B organic materials. If the energy band bending is not considered, the near interface electric field does not appear [4,10]. Indeed the driving force to separate (e–, h+) electrical charges is absent within the currently accepted photosynthesis mechanism model [13,15]. But experimental and theoretical work has shown the opposite and band bending should be considered [11,35-38].

The electronic states of Donor/Acceptor interfaces and the simplified HOMO/LUMO diagrams presented in the literature have generally been described, considering the electron donor and electron acceptor components in their isolated form [13,15]. However it neglects the specific electronic interaction at the Donor/Acceptor interface related to electronic polarization effects (expected to be different at the interface from the donor or acceptor bulk material) and possible charge transfer from donor to acceptor molecules [35]. However if charges transfer is universally accepted (this the origin of photovoltaics), why the interface (e–, h+) recombination of these charges is not frequently considered? Moreover, if charges transfer is universally accepted, why it is not recognized/accepted the electronic non-equilibrium on both sides of the interface? Otherwise violation of physical laws is present and accepted, behind a supposed "controversial" argument. The A/B interface recombination/emission can be related to the spent energy to separate electrical charges from the interface within organic molecules in plants.

Figures 2-4 represent a proposed scientific physical energetic configuration to explain the natural photosynthetic first step mechanism. A/B being an organic composed interface. This is the only energetic interface configuration (if excited) able to separate electrical charges of different polarities (and under attraction) [4,12,23-25, 31]. According to the physical need of electric field to separate e– from h+, the interface electrical fields $\mathbf{E_{iA}}$ and $\mathbf{E_{iB}}$ (**Figure 2**) support this proposition. Moreover it presents the driving force and the spent energy for (e–, h+)

charges separation. Even in Nature it is necessary to spend some energy to perform an activity. Most of the plants on Earth are green colour, but less of them extend to yellow, brown and red colour intensities, depending of the internal leaves architecture (physical and chemical properties) [2]. This molecular architecture is about 1 nm and, according to this, the presented interface energy levels should be more pronounced numerically, allowing much broader interface emission (increasing ΔQ_e and ΔQ_h on **Figure 3**). These A/B interface emissions can be related to the colours emission seen on leaves. Thus the colour of leaves should be considered mostly an emission, when considered the spent energy to separate electrical charges of different polarities. It means that these emission colours' should be mostly related to the spent energy performing the first physical step to separate (e–, h+) electrical charges. On plants we have scattering (transmission and reflection) and emission components [15,39,40]. The spent energy emission we mention is for the charge separation mechanism and not for the total colour of plants. Indeed blue, green, red colours emissions have been experimentally observed in plants by many authors [39-42]. Why plants are green is still an open question [41]. There are many evidences that the green leaves absorb more efficiently light of green (550 nm) than blue (480 nm) spectra [42]. The absorbance for the 550 nm range is 50% for lettuce, to 90% in evergreen broad-leaved trees. Green light is more penetrative (*i.e.*, reach all leaf thickness) than blue or red light, absorbed mostly on the upper part of the leaf. This is the reason why the green light is more efficient for the photosynthesis process in plants [42]. Moreover, if the green colour is more efficient than blue and red colours, to perform the photosynthesis process, why to consider the green colour of plants as a reflection [42]? Note that reflection is not considered as an interaction with the leaves' molecules. If the green colour of plants is also presently related to the charges separation mechanism, few changes in the gene expression should be operated when leaves molecules have they environment changed [43,44].

If current natural conditions for plants are to spend energy mostly on the green colour spectral region, in the past this colour could be on another spectral region (maybe red shifted), to account for the huge amount of petroleum we have today, originating from exuberant forests from 600 - 700 millions of years ago. If sugarcane plantation in its natural colour (green) can be genetically yellow coloured (red shifted), we should have $(h\nu_{green} - h\nu_{yellow})/h\nu_{green}$ ~19%, which represents the energy economy for the sugarcane machinery to work out its internal processes and to produce more biomass and/or sugar. But it is only possible if the colour can be related to an emission for the natural photosynthetic mechanism and related mostly to the spent energy to separate electrical charges.

Breeding plants have other lower intensities for colours emissions [2]. Changing Earth atmospheric conditions (e.g., concentration of CO_2, O_2, H_2O, CH_4, NH_4, acids) will determine the plants adaptation for their size, colour, nutritive power and exchange with the environment. Indeed, by changing the CO_2 (2×390 ppm) concentration available to the sugarcane environment, it can be increased by 60% the biomass and 25% - 30% the sugar content [44]. Moreover gene expression is accordingly changed [44]. These authors does not mention sugarcane colour change but they mention the possibility of gene expression alteration to be related to charges transport and CO_2 assimilation by sugarcane [43,44]. If gene expression is associated to charge transport, it is surely linked to the charges separation mechanism, discussed above.

Recently Yen Hsun Su and co-workers, doping plants (*in vivo* experiment with *Bacopa carolinianais*) with gold nanoparticles, showed that it is possible to change the colour of leaves to red, yellow or blue, depending on the excitation light and the gold nanoparticle size/shape [45]. Exciting the *Bacopa carolinianais*/gold system with white light they have obtained yellow leaves. Exciting the same system with UV (285 nm) they have obtained blue and red coloured leaves. If in *Bacopa carolinianais* leaves the green colour is a reflection, due to Chl-a, the leaves should keep green. It means we cannot extract Chl-a from leaves and conclude that "plants are green because Chl-a does not absorbs green light". Gold nanoparticles change the Chl-a environment, changing the emission colour, and the Chl-a is still there. If Chl-a is still there and we cannot consider the colour as reflection anymore, what should be the Gold/Chl-a red or blue colour mechanism: an emission or a reflection?

Other experiment developed by Blitz and co-workers, by changing lettuces environment, exposing it to more UV (A + B) energetic light, it was observed the colour change [46]. Moreover two times more nutritive power for these UV (A + B) extra-exposed lettuces was observed. Gene expression change should follows in these experiments, as it is the case of the sugarcane [43,44]. Furthermore on an old article on green fluorescent proteins (GFP), it is proposed that the two visible absorption bands correspond to "two ground-state conformation" [47]. The staggered band gap relative position has "two ground-state like" energetic conformation, as proposed on **Figures 1** to **3**. On support information 4, [SI 4], we present few experiments on plants, showing that leaves have their internal machinery that transform high energy photons into lower energy photons (red shift). The absorption of light and emission at lower energy is proposed to perform the charges separation process.

Studies with organic LEDs and organic solar cells apply the concept of staggered energetic configuration to produce or to absorb light [48-57]. These organic devices

are emitting/absorbing light and replacing solid state LED/solar cell, respectively. The organic light emitting/ absorbing are composed of tens of nanosized layers of few tens nanometer thickness. Organic molecules are diluted in a medium and these molecules touch each other at the layers' interface. A. Heeger (2000 Chemistry Nobel Prize Laureate) used staggered energetic organic/ organic interfaces to produce about 10% efficiency solar cells [52-54]. The energy peak emission at these staggered energetic interfaces and layers are broad and intense [48-60], a characteristic of type II staggered interface energy emission, as represented in **Figures 5** and **6** and discussed above.

In this paper we discuss the band gap energy emission whenever energetic A/B interfaces are present. As Fluorescence Resonance Energy Transfer (FRET) mechanism deals with below band gap emission, we will equally propose few words about the possibility of its explanation be regarded as type II interface emission. Note that FRET model is based on classical physics, described/proposed about 60 years ago by Theodor Forster [13,61]. FRET model suffers from few drawbacks, considering unknown parameters, correction factors, intensities corrections, etc [62,63]. Based on our results, a different model can equally be proposed to explain the "energy transfer" between two different organic or inorganic material pairs, based on the existing and actual band gap energy relative position of both A/B pairs. According to recent experimental works, organic molecules present energetic steps (up or down) for excited electrical charges to travel from a molecule to another one [48,60]. These energetic steps for electrical charges flow, from a molecule to a nearby molecule, are very important and not considered on the FRET theory. These energetic steps can promote energy interface emission (red shifted), observed for many published data explanation. As FRET is a radiationless energy transmission mechanism, we propose that the actual physical/ optical mechanism can be regarded as a radiation interface emission mechanism, for many systems, based on type II interface properties. As an example, the application of the present proposed model can be applied for cyanide dyes (Cy3, Cy5) organic molecules [62,63]. When these molecules pairs are placed together, forming a Cy3/Cy5 interface, an emission peak at 680 nm is observed, when excited with 540 nm light [62 and SI-3]. This 680 nm emission of the Cy3/Cy5 system can be associated to type II interface emission. In this way, FRET should deeply be re-discussed as it is based on classical physics and staggered energetic interfaces are based on quantum physics.

In this paper, type II interface energetic configuration and interface emission is proposed to explain electrical charges separation. It can equally be proposed to explain many non-comprehensible physical observation like FRET, GFP, green colour of plants and its colours changes by changing the proteins environments [48-60,63]. The mechanism, based on type II interface, is supported by the quantum mechanical basis, in contrast to the classical theory used to explain the photosynthesis first step (charges separation), GFP and FRET. Note that FRET mechanism doe not separate electrical charges. Only the absorption of light is not enough to separate electrons from holes. A question comes about: If FRET is present on the photosynthesis process, where is it, the charges separation mechanism?

Many recent experimental studies propose the photosynthesis process as quantum mechanics controlled [64-71]. Forster's theory is based on classical physics; moreover it is based on a non-existing energetic configuration, as is the case for the GSE representation [4,10,13,15]. Forster theory does not present the necessary electric field to separate electrical charges. It does not present the spent energy to perform this process [13,15]. In summary, the present classical theory violates physical laws, concerning the necessary tools to separate electrical charges under attraction.

In conclusion to this section, we propose the staggered energetic interface (quantum mechanics controlled) to explain the photosynthesis, FRET and GFP processes, instead of the ground state energy (classical physics description) configuration. The staggered configuration has been used between organic molecules to produce organic LEDs and organic solar cells. The staggered configuretion and energy band bending for organics is a real physical property and not a controversial language. It gives us the necessary physical tools to separate electrical charges. If recent optical experiments propose photosynthesis as a quantum mechanics controlled, we should look for quantum physics instead of classical physics. The use of the ground state energetic configuration, to explain the photosynthetic mechanism, is a non-sense physical pathway that should be re-discussed. Under photons excitation, charge's jumping to the nearby organic molecule brings the near interface to a non-equilibrium condition, on both A and B molecules' electronic structure. The non-equilibrium brings energy band bending (or potential variation) and Fermi level movement (dynamic process). As the A/B generic organic systems are nanometer size and distances, each (e–, h+) wavefunctions should cross few molecules under interaction. It is impossible not to consider this fact on natural systems. Note that the staggered energetic configuration can be present at the same organic molecule, as it can be for two different molecules. This molecule can be branched composed, representing an energetic interface of the three types describe above, but never with the GSE configuration.

9. Application of the Charge Separation Mechanism: How to Waste the Visible Light Absorbed Energy by Leaves

Electrical charges separation mechanism is not yet well understood for photosynthetic natural and artificial applications. The present preliminary proposition represents a new regard on the photosynthetic natural and artificial electrical charge separation mechanism. Considering it as a new mechanism, most of the parameters necessary to calculate the efficiency (number of separated charges/ number of photons) are not available. According to the present model, it can also be applied to other materials presenting staggered energy configuration, the polymer/ polymer and polymer/inorganic interfaces [49-60]. It can equally occur with the exciton dissociation transferring a single charge to the material A, leaving behind an opposite charge in material B [22,34,51]. Excitons from electrical charges seated on different materials are different from excitons seated within the same material. The authors are not aware about experimental/theoretical results/ values of excitons when electrical charges of different polarities are seated on different materials or molecules [10,22]. The charge transfer (number of charges/number of photons) for photovoltaics, of about 1% - 6% efficiency, is easily achieved for nanostructured materials [8,10, 16-21]. The same condition is valid for photovoltaic organic/organic or inorganic/inorganic solar cells, in which about 10% efficiency is commonly achieved [10,52-57]. As the material's properties and its interfaces have an important role, the present model should be applied and improved to increase devices efficiency. Note that the organic/organic interface for LEDs and solar cells uses the staggered energetic configuration, instead of "ground state energy" configuration and that this model cannot be considered as a controversial subject [32-36,49-60].

Concerning the natural photosynthesis, the sunlight energy absorption and the final efficiency by leaves on plants seems to be about 5% [1-3,13]. In this way the application of the present model to estimate the charge separation efficiency needs new experiments, because most of the available data concern non-staggered energetic configuration (the GSE one). Moreover the green colour of plants is considered mostly a reflection. It should be emphasised that green leaves have also other minor colours intensity (emission?), such as yellow, brown and red [2]. If these lower intensity colours represent also charges separation within a leaf, caused by a staggered configuration between the energy bands of leaves' constituents, the efficiency should be verified in consequence. When it occurs, the natural leaves' constituents should propose many staggered energy configuretion. Chl and carotene present 3 - 5 main absorption energy peaks [2,13,15]. More efforts are needed to find out the actual energy relative position for each absorption energy band for the leaves' constituents. To know their energetic relative position, more studies are necessary on the band gap engineering to present the actual energetic configuration and both: charges separation and waste of energy to perform the job.

Transmittance (T) and reflectance (R) experiments on leaves, within the 400 to 700 nm spectral region, give scattering (S) of about 21% (S = T + R), according to many previous standard experimental results [15,72]. **Figure 8** concerns typical reflectance and transmittance curves for leaves, on the visible (400 - 700 nm) and infra-red (700 - 1000 nm) spectral regions, showing the necessity for plants to have an efficient way to waste the sun light energy quickly. Maybe the staggered interface is the only appropriate candidate. The absorption experiments for isolated Chl-a cannot evidence scientifically that leaves do not absorb on the green region. They represent different systems. Moreover transmittance and reflectance experiments show that leaves reflect on the green colour about 15%, as presented on **Figure 8** [15, 72]. The transmittance is about 30% for the 535 nm green spectral region. It means the absorbance is about 55% for the green (535 nm) colour region. 15% for the reflection cannot explain the green colour intensity of plants. Type II interface can be able to absorb and emit nearly the same light wavelength [73]. In this case, the absorption is carried out by an excited electron jumping directly to the nearby material (VB of B material to the CB of A material, **Figure 3**) [73]. The de-excitation of this electron is followed by the interface emission, emitting about the same colour or energy that is absorbed (**Figures 2** and **4**). Note that interface absorption should create energy band bending on both sides of the A/B interface.

According to **Figure 8**, for the visible region (400 - 700 nm), the area below T and R curves gives scattering S = T + R = 21%. As % Absorbance = 100% – (R + T), on average, 79% of the visible spectra is absorbed by leaves, representing a huge amount of energy that plants cannot afford. Nature should invent an efficient way to waste quickly this absorbed sunlight energy. Type II energetic interface can be a good candidate, wasting it as an emission, but related to the spent energy to separate electrical charges, a non-efficient quantum mechanism to separate (e–, h+) electrical charges.

Maybe nature have got the solution and created type II interface as the mechanism to get ride of most of the 79% average absorption within the 400 - 700 nm solar range (**Figure 8**) [15,72]. So, if natural photosynthesis efficiency is about or below 5% it should be withdraw from 79% absorption, for the 400 - 700 nm visible solar spectra. Artificial photosynthetic nanomaterials get about 1% - 6%

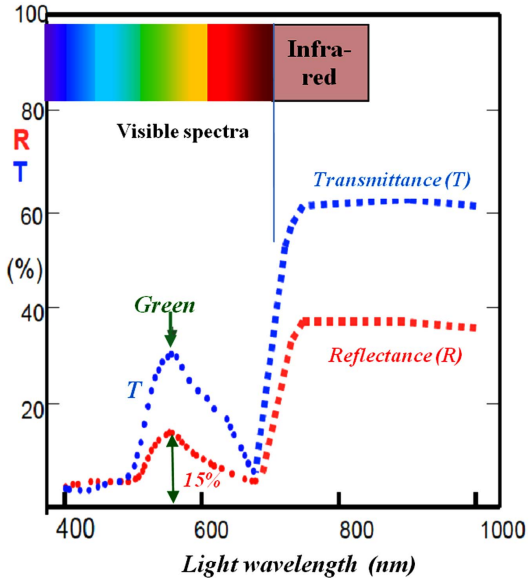

Figure 8. Typical reflectance and transmittance curves for leaves on the visible and infrared spectral regions, evidencing the necessity of an efficient way to waste quickly the sun light energy for plants. Note that there is only 15% of reflectance on the green colour region (535 nm). The R + T value at the 400 - 700 nm region gives an average absorbance of about 79%. This is a huge value to be afforded by plants in hot lands. Average values were obtained from the area below the R and T curves, for the desired spectral region. R + T is about 98% within the infrared region. There is almost no absorption for the IR region, for plants. The typical R and T results are extracted from references [15,72].

efficiency for their transformation from photons to separated electrical charges [8,16-20,27-29]. **Figure 2** and support information 1 [SI-1] show the interface recombination/emission is a mechanism to get charges separation [9,12,23-25,30,31]. Moreover, it is not an efficient mechanism to separate electrical charges, because most of the excitation light energy is spent as interface emission. The artificial photosynthetic literature had never touched and related the interface emission as a consequence of the low efficiency of the explored devices (1% to 6% efficiency) [8,16-20,27-29]. Here we propose the interface emission mechanism to account for most of these low efficiency natural or artificial devices.

In conclusion to this section, according to published data, natural leaves should absorb about 55% of the sun green spectra in the visible region. 15% of reflection does not explain the green "reflection" colour intensity of plants. As leaves absorbs higher photons energy than the green photons and emit lower energy photons (green, yellow, red), to the green colour intensity of leaves it should be added the green transformed by their internal machinery. According to the same published data, leaves should absorb, on average, 79% of the visible sun light spectral region. This enormous quantity has never been discussed in the literature and should be able to cook plants in few minutes on sunny days. It means that we need a quick and an efficient optical mechanism to get rid of this cooking absorbing system. The same consideration is valid for artificial photosynthetic systems, for which efficiency is low (1% - 6%). Type II energetic interface and its interface emission is the only possible configuration to solve the problem: a really efficient way to absorb and waste photons, meanwhile separating few % of the excited (e–, h+) charges.

10. Final Considerations and Conclusions

To copy the photosynthetic natural conditions we need to use existing physical conditions that explain the charges separation mechanism. Currently natural photosynthesis mechanism accepted model is not scientifically and physically acceptable: the energetic configuration does not hold on physical basis and neither allows the current physical situation to separate electrical charges with different polarities (or charges under attraction). Artificial nanostructured photosynthetic materials models suffer from the same scientific physical drawback: the mechanism to separate electrical charges under attraction.

In few words, both natural and artificial models violate physical laws if they are not able to present the necessary electric field (the driving force) and the spent energy to separate negative (e–) from positive (h+) charges. Correcting these common related drawbacks we can further improve artificial and natural photosynthetic systems and get more energy from the free sunlight source. The solar energy is our only economical pathway if the physical mechanism underling the 2 - 4 billions years of evolution is understood: the charges separation mechanism. If nowadays the solar energy is less efficiently used than in the past (600 - 700 millions of years ago, with a more elevated CO_2 concentration) for the natural conversion into fuel, we get to a controversial question: is the desertification a direct consequence of the CO_2 atmospheric concentration decreasing (200 - 370 ppm, years from 1850-2010) [1-3]? If so, the greenhouse effect should be observed differently from current point of view. To this end, the natural and artificial energetic configuration between two different materials should be correctly considered. Excited A/B materials and interfaces can deliver the necessary driving force to separate electrical charges charge (charges with different polarities). The currently defended staggered representation for the II-VI/II-VI and TiO_2/II-VI nanosystems, to separate electrical charges, does not present any physical support to separate e– from h+ [16-21,27-29,79-85]. Indeed, these very important experimental results does not explain correctly how electrical charges flow as they were gravitational-like balls falling down through stairs [16-21,27-29,73-88]. Unfortunately electrical charges should obey electrical parameters.

The misunderstood on electrical charges separation mechanism has been propagated for many published results [27-29,73-87]. Commonly found assertion like "*... the absorption of a photon leads to efficient separation of a single electron-hole pair*" is present in the literature, without scientific care [80]. The absorption is only the first step. The subsequent step, to separate (e–, h+), should spend energy. Interface energy band bending has equally been proposed erroneously, even using type II interface to explain electrical charges separation and its flow direction [74,75]. The staggered energy configuration and its band bending should be downwards and not upwards as recently published [74-78]. Basic physical information on electronics and solid-state physics is available everywhere and has been constantly neglected [4-7,10,22]. Interface emission has been erroneously attributed to "charge transfer state", for organic and inorganic systems, meanwhile it is just a recombination of e– with h+ seated on different materials [27-29,51,77,88].

Most of the published data and mechanism explanation uses the flat band configuration to show e– and h+ movements across the interface between an A/B generic interface [13,15,27-29,48,77-88]. This is proposed for organic and inorganic generic materials [27-29,77-88]. These published work do not consider the energy band bending as exposed above and as exposed in many solid state physics and organic material published data [4-7,9,10,12, 22,36]. The electrical charge jumping from a material to the nearby material creates an electronic non-equilibrium on both materials, moving the quasi-Fermi level (up or down) and, consequently, moving the CB (LUMO) & VB (HOMO) (down or up) [4,10,SI-1].

In summary, it is proposed a model describing the only energetic configuration between two different nanosized materials, able to provide the necessary electric field to perform (e–, h+) electrical charges separation on photovoltaic systems, such as inorganic/inorganic, inorganic/organic and organic/organic interfaces. It is presented, in these descriptions, many systems in which type II interface recombination and emission is the most important electro/optical phenomena: AlInAs/InP, TiO_2/II-VI and II-VI/II-VI. These experimental results have been linked to organic solar cells and organic LEDs, in which the staggered energetic configuration is experimentally already known and applied. We have shown that the optically excited AlInAs/InP system has an internal electric field ($\approx 10^5$ V/cm), issued from the energy band-bending whenever charges jump to the nearby material. The ground state energy (GSE) representation, to explain photosynthetic mechanisms, is a non-existing physical energetic configuration. Charges do not care about GSE, charges care about energetic steps if the aim is to separate electrons from holes. GSE model does not allow the separation of e– from h+ because it does not promote the basic electric field and the spent energy to separate charges under attraction. Without these two basic physical concepts it is impossible to separate (e–, h+) electrical charges in nanosized materials without violating physical laws. Contrary to current believes, charges do not get separated whenever nanomaterials absorb light. This is only the first step and it represents an excitonic attractive entity. The next step, to separate (e–, h+), depends on energetic configurations under which these charges are submitted. Diffusion controlled process on nanometric systems is out of question. Diffusion controlled processes is for the old generation of silicon devices (about 1 μm diffusion length). The proposed model, based on staggered energetic interfaces and energy band bending, introduces equally the concept of spent energy to separate electrical charges. The spent energy is related to the interface emission and it can be used to explain most of the photons emission of absorbed visible sunlight (~79%) by plants. It is impossible the surviving of plants without an efficient and quick (optical) way to waste the absorbed visible light. Moreover, the proposed mechanism is quantum controlled, as proposed by many recent experimental results on organic molecules. According to published data, it was shown that, by changing the plants' environment, there will be change in the biomass and nutritive power. Similarly, by changing the leaves' molecules environment, the leaves' colour also change. In this way, the colours of plants can be mostly related to the spent energy to separate electrical charges. The green colour being more efficient to promote the photosynthesis process, instead of being a reflection, without relationship with the process, can be linked to the charges separation mechanism: it can mostly be linked to the waste, to perform the process and to protect leaves. The ideas and results presented here can be extended to other models or materials/devices as FRET, GFP, CTS, organic LED and organic solar cells. Human needs to know this Nature non-efficient charges separation mechanism to improve its efficiency in natural and in artificial solar energy production. The energetic staggered configuration is an appropriate candidate. But it should be worked out with its intrinsic physical parameters, already described in the literature, but not correctly considered by many photosynthetic workers. If worked out correctly, natural and artificial photosynthetic systems can be adequately copied/improved. Nature obeys physical principals. Men should follow this way, in trying to explain natural and artificial physical mechanisms. Charges separation is a physical and not a biological mechanism.

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Support Information

SI-1. Energy Staggered Interface: Electrical Charge Separation Mechanism

Résumé

The following slides present how the proposed mechanism does work, based on the excitation of one hypothetical interface between (Material A)/(Material B). This excitation is performed with only 4 photons. It is, equally, represented why the interface recombination/emission process has a so large emission peak. The (e–, h+) wavefunctions penetration is represented for the AlInAs/InP system. The present SI-1 should be viewed in a ppt version by clicking below. **Figure SI-1-1** represents energy band bending mechanism. **Figure SI-1-2** represents the jumping of charges to the nearby material. **Figure SI-1-3** represents the separated charges and its catalytic action. **Figure SI-1-4** represents the two quasi-triangular quantum wells at the interface, to explain the interface emission peak broadness. **Figure SI-1-5** represents the two quasi-triangular quantum wells at the interface, to explain the e– h+ wavefunctions overlap.

Comments

The natural photosynthetic first step process is based on the light absorption and followed by electrical charges separation on leaves. Only the absorption of light does not separate e– from h+. The absorption of light creates (e–, h+) pairs. For the separation we need an appropriated energetic configuration.

The present existing Forster's model, to explain the photosynthetic first step process, is based on classical physics. The same ideas are applied to artificial systems. The present accepted model violates mainly three physical laws.

1) The energetic configuration, that represents the energy transfer from a molecule A to a nearby molecule B, does not exist in physics (the ground state energy representation). Charges do not care about the ground state energy configuration. Charges care about energetic steps (up or down).

2) To separate negative from positive charges, the necessary electric field is not present. The absorption of light does not separate electrical charges. This is just the first step of the process. To do the next part we need an appropriate energetic configuration that allows the apparition of the electric field. This electric field must come from a varying potential.

3) To separate electrical charges under attraction we must spend energy. Note that the excitonic attraction energy between e– and h+ on organic molecules is about 10 to 50 times that ones present on inorganic materials. This means that we need a much stronger electric field for organics, to separate (e–, h+). Moreover, recent papers (about 10), published in Nature, Science, PRL, (see text), show evidences that the photosynthesis first step mechanism is quantum mechanics controlled.

The enclosed and proposed mechanism does not suffer from these drawbacks (1 to 3). It is a photonic quantum mechanics mechanism.

Click here to see the ppt slow motion model.

Note: the ppt pictures were prepared in a Machintosh computer. Version:

SI-2. Mathematics Calculus (Wavefunction, Probabilities Densities)

Résumé

The following pages present details of the calculations

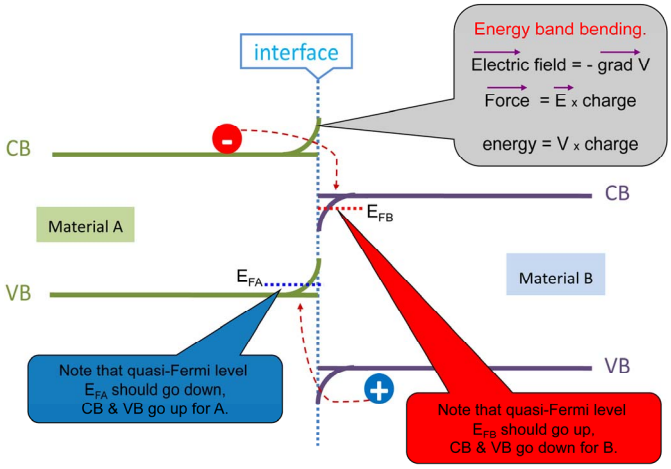

Figure SI-1-1. Representing the energy staggered interface: electrical charge separation mechanism. How does the energy band bending arrive at the energetic interface? The flow of charges from one material to the nearby material creates an electronic no-equilibrium on both materials, near the interface. This electronic non-equilibrium creates potential variation. It creates the necessary electric field to separate charges: e– from h+.

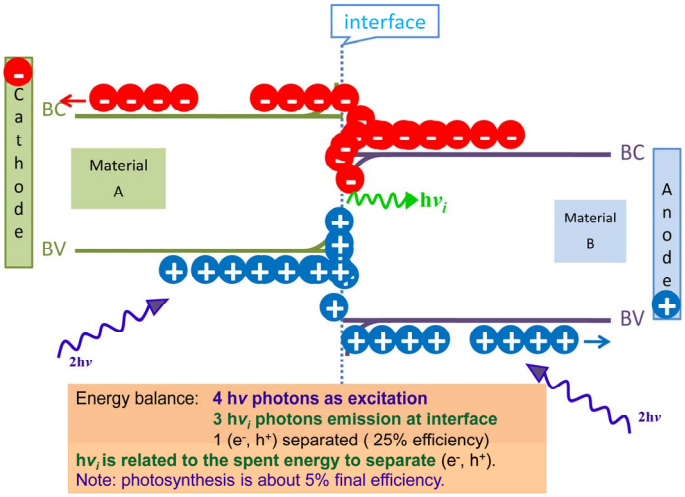

Figure SI-1-2. Representing the energy staggered interface. It represents the charge separation mechanism in a picturial slow motion maner. Excitation of such an energetic structure with only 4 photons.

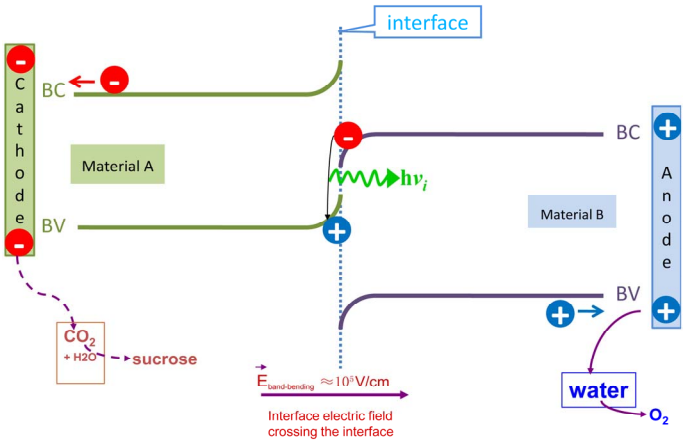

Figure SI-1-3. Representing the energy staggered interface: charge separation mechanism applied to photosynthetic first step processes. Note the hudge electric field crossing the interface for the AlInAs/InP system (see text). For organic molecules, this electric field should be much higher since the excitonic attraction is much higher than for inorganic materials.

Why is the interface emission peak so large? See it in the nexts slides…

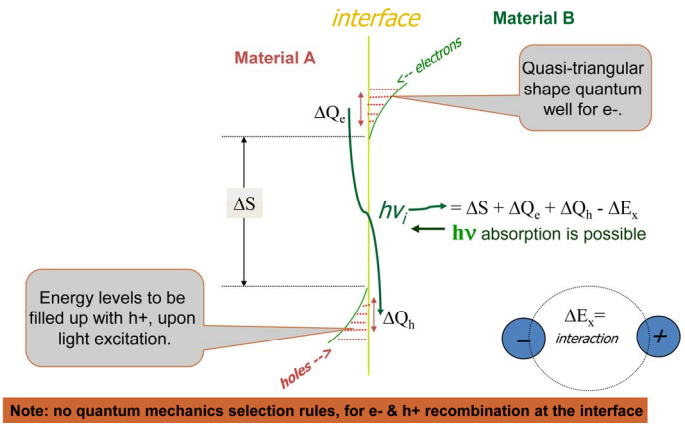

Figure SI-1-4. Representing the interface physical parts linked to the interface emission peak. All the terms of the equation below should change with the excitation intensity. Mainly $\Delta Q_e + \Delta Q_h$ should change more than the others terms. This explain why the interface PL & EL emission peaks' are so large.

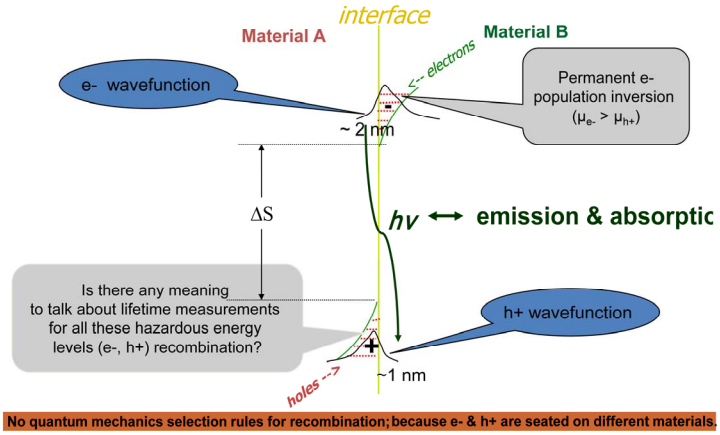

Figure SI-1-5. Representing the interface physical parts linked to the interface recombination/emission peak. The interface recombination and emission depends on the e− & h+ wavefunctions' interface overlap. The 1 to 2 nm wave-function penetration is for the AlInAs/InP system (see text).

for the probability density and the (e–, h+) wavefunction overlap at the AlInAs/InP interface. In this work the bands are modelled as exponential bended bands, leading to Bessel wavefunctions for carriers. Energy levels of carriers at valence and conduction bands, as well tunnelling length, for each kind of carrier are calculated by solving the transcendental equation obtained for wave function continuity at the interface. Parameters for the present calculation were taken from reference. Abraham, P. et al. Photoluminescence and band offsets of AlInAs/InP. Semiconductor Sci. Technology **10**, 1-10 (1995) [23].

Comments

The photon excited staggered AlInAs/InP interface gives rise to an interface electric field of about 10^5 V/cm. This is approximately the same value obtained for the experimental result of **Figure SI-2-1** (see text). The calculated e– wavefunction penetration on the AlInAs material is about 2 nm. The calculated h+ wavefunction on the InP material is about 1 nm. Both values account for the interface (e–, h+) recombination and interface intense emission.

Both bands of valence and conduction bands have similar, bent on account of them injected carriers. In each of the potential will be approximated by exponential functions as shown in Equation (1) and picture in **Figure SI-2-1**.

$$\begin{aligned} V(x) &= V_o + \delta\left(1 - e^{-x/\sigma}\right) \quad x \geq 0 \\ V(x) &= V_1 - \Delta\left(1 - e^{x/\eta}\right) \quad x < 0 \end{aligned} \tag{1}$$

Substituting these potentials in the Schroedinger equation we have:

$$\begin{aligned} &\frac{d^2\psi}{dx^2} + \frac{2m^*}{\hbar^2}\left\{E - \left[V_o + \delta\left(1 - e^{-x/\sigma}\right)\right]\right\} \psi = 0 \quad x \geq 0 \\ &\frac{d^2\psi}{dx^2} + \frac{2m^*}{\hbar^2}\left\{E - \left[V_1 - \Delta\left(1 - e^{x/\eta}\right)\right]\right\} \psi = 0 \quad x < 0 \end{aligned} \tag{2}$$

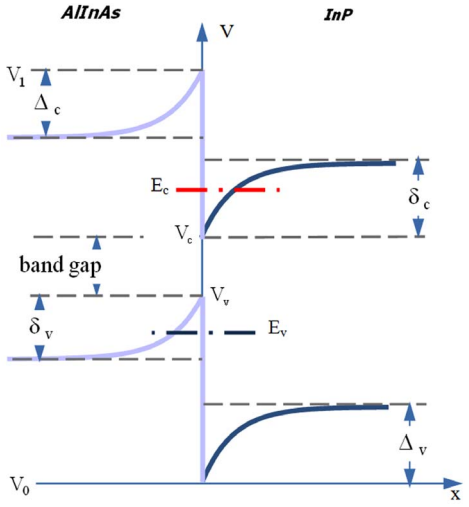

Figure SI-2-1. The scheme of tilted electronic bands for AlInAs/InP.

These equations are applied to both the calculation of energy levels for the holes in the valence band and for the electrons in the conduction band. In each case we should observe the proper values of the parameters of the **Table 1**. Using the transformation of variables

$$\begin{aligned} \xi_+ &= \left(2\sigma\sqrt{\frac{2m^*}{\hbar^2}\delta}\right) e^{-x/2\sigma} \\ \xi_- &= \left(2\eta\sqrt{\frac{2m^*}{\hbar^2}\Delta}\right) e^{x/2\eta} \end{aligned} \tag{3}$$

We get the following equations:

$$\begin{aligned} &\xi_+^2 \frac{d^2\psi}{d\xi_+^2} + \xi_+ \frac{d\psi}{d\xi_+} + \left(\xi_+^2 - 4v^2\right)\psi = 0 \quad x \geq 0 \\ &\xi_-^2 \frac{d^2\psi}{d\xi_-^2} + \xi_- \frac{d\psi}{d\xi_-} - \left(\xi_-^2 + 4\mu^2\right)\psi = 0 \quad x < 0 \end{aligned} \tag{4}$$

These are the known Bessel equations in which it is defined the parameters:

$$\nu^2 = \frac{2m^*\sigma^2}{\hbar^2}\left[\left(V_o + \delta\right) - E\right]$$
$$\mu^2 = \frac{2m^*\eta^2}{\hbar^2}\left[\left(V_1 - \delta\right) - E\right] \quad (5)$$

The solutions for the Equations (4) will be:

$$\Psi_+(x) = \mathrm{A}\mathrm{J}_{2\nu}(\xi_+) \quad x \geq 0$$
$$\Psi_-(x) = \mathrm{B}\mathrm{I}_{2\mu}(\xi_-) \quad x < 0 \quad (6)$$

These solutions must satisfy the boundary conditions at $x = 0$. Equating the functions and their derivatives at $x = 0$ results the transcendental equation:

$$\frac{\nu}{\sigma}\frac{\mathrm{J}_{2\nu+1}(2\nu)}{\mathrm{J}_{2\nu}(2\nu)} = \left(\frac{\sigma\mu}{\nu\eta} + \frac{\nu}{\sigma}\right) + \frac{\sigma u}{\nu\eta}\frac{\mathrm{I}_{2\mu+1}(2u)}{\mathrm{I}_{2\mu}(2u)} \quad (7)$$

The probability density is represented by

$$\mathrm{P}(x) = \left|\Psi(x)\right|^2 \quad (8)$$

The parameters concerning the potential wells in the conduction band and valence are those given in **Table 1**.

Solving the transcendental equations for the valence and conduction bands it was obtained two energy levels for holes (VB) and one energy level for electrons (CB) in the conduction band. The energies and the parameters that determine the wave functions for electrons and holes are given in **Table 2** and the density probabilities are represented in **Figures SI-2-2** and **SI-2-3**.

SI-3. Fluorescence Resonance Energy Transfer (FRET), Presented as Type II Interface Emission

Résumé

The following pages present how the proposed mechanism does work for FRET. Fluorescence resonance energy transfer (FRET), is a physical phenomenon by means of which electronic excitation can pass from one chemical unit to another, following the absorption of light. The chemical unit we are discussing here is only for chromophores. In this support information, FRET is observed as a type II interface emission and not as an energy transfer from one material to the nearby material. It is presented just one example for organic cyanine dyes molecules. The same idea can also be applied to green

Table 1. Parameters for the potential wells.

V_o (meV)	V_1 (meV)	δ (meV)	Δ (meV)	σ (nm)	η (nm)	m_e
0	349	60	20	5	5	0.07
0	272	60	20	5	5	0.4

Table 2. Energies and parameters determining the wave functions for electrons and roles.

	A	B	E (meV)	V_1-E(meV)
Electrons	0.491	804.794	54.68	5.32
Holes	1.223	5.313×10^5	38.85	232.68
	0.689	-9.9×10^4	56.13	215.87

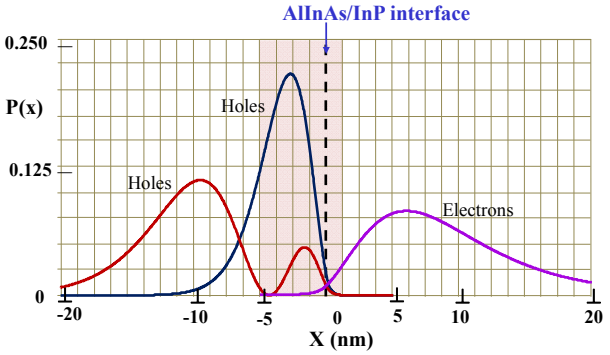

Figure SI-2-2. It shows the probability density versus distance within the structure, for the valence band and conduction band, where we see that the penetration probability for electrons and holes beyond the wall of the well. The region with interpenetrating wavefunctions is pointed out in the figure by pink colored rectangle.

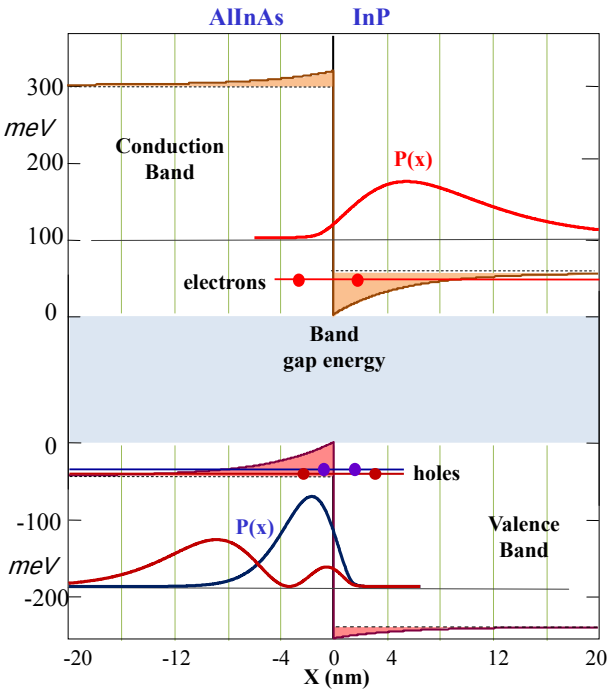

Figure SI-2-3. It shows schematically, with the values of the energy-scale the probability densities for electrons and holes relative to the potential wells within the system AlInAs/InP. X (nm) is the distance from the interface.

fluorescent proteins (GFP) as well. These ideas are presented on **Figures SI-3-1**, **SI-3-2** and **SI-3-3**. They have the explanation text for each one figure.

SI-4. Experiments with Leaves

Résumé

The following pages present how the proposed mechanism does work for leaves from plants. This SI presents experiments with leaves, showing their internal transformation machine, absorbing higher energy photons and emitting lower energy photons. Leaves are considered to have about 1 nm size proteins, separated by about 1 nm distance. These dimensions give about 10^{20} energetic interfaces/cm^3. This is above the doping density (10^{17} to 10^{18} atoms/cm^3) for inorganic semiconductor optical devices or organic optical devices. These numbers show that interface must be taken in to consideration if absorption/emission mechanisms are discussed for leaves.

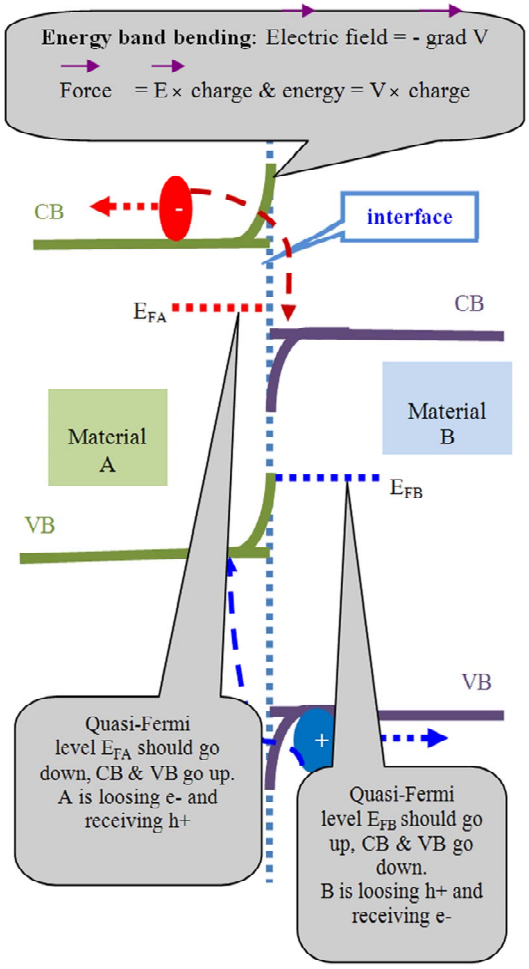

Figure SI-3-1. Representation of an A/B type II generic interface, showing the motion for the energy band bending and the quasi-Fermi levels displacements, whenever the A/B system is excited by photons which energy is higher than both A & B materials' band gap. At the interface, the energy staggered interface (type II): electrical charge separation mechanism, by an existing interface electric field. This electric field comes from a varying potential, which origin is from the energy band bending at the interface. Whenever charges jump to the nearby material, the electronic environment is changed in both materials. This change creates the potential variation and the interface electric field. This interface and its properties are applied to explain FRET.

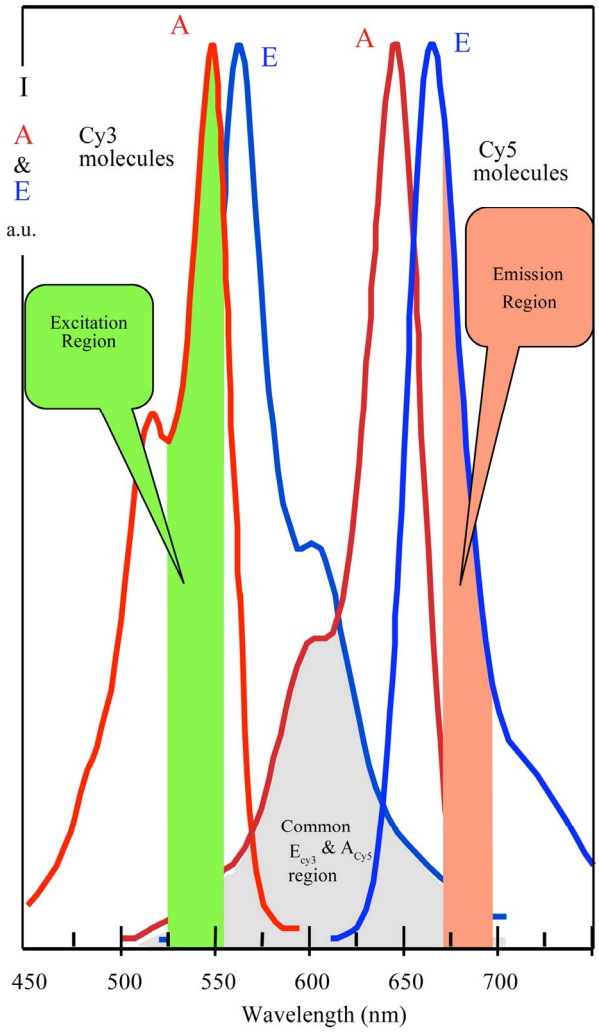

Figure SI-3-2. Intensity (I) versus wavelength (λ) for optical properties of cyanides molecules. Representation of the absorption (A) and emission (E) regions for Cy3 & Cy5 organic cyanine dyes [62,63]. The dashed common region represents the overlap between the Cy3 emission region and the Cy5 absorption region of these molecules. Following FRET mechanism, the common A & E region for both molecules allows the Cy3 molecule be excited on the 525 - 550 nm region and the Cy5 molecule to emit within the 670 - 700 nm region. This red-shifted emission is proposed to be type II interface related in the next Figure SI-3-3.

Comments

We performed optical absorption (**Figure SI-4-1**) and

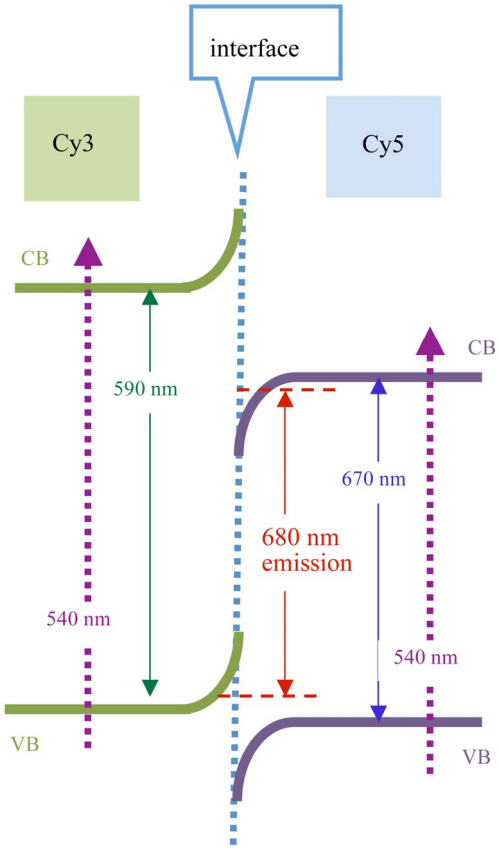

Figure SI-3-3. Representation of a type II interface. Instead of FRET, it is explained by energy staggered configuration interface emission. 540 nm is related to the external excitation energy. 680 nm is related to the interface emitted energy. 590 nm is related to the Cy3 main bandgap energy and 670 nm is related to the main Cy5 bandgap energy. Organic cyanine dyes: Cy3 = A and Cy5 = B [62,63]. Note that the present proposal (type II energetic configuration) does not need momentum conservation, as is the case for FRET. Symmetry (QM selection rules) does not apply since both e– & h+ are seated on different materials when they recombine.

photoluminescence (PL, **Figures SI-4-2** and **3**) experiments on leaves (*Erytrina indica picta*) at room temperature, to see if there are emissions from them. These leaves are naturally composed of green and yellow regions (**Figure SI-4-1**). We used intact young yellow-green *Erytrina indica picta* leaves exposed to green (532 nm) and violet (386 nm) laser light excitation. The leaves' regions exposed to these excitation wavelengths resulted in broad-band light emission on the blue, green, yellow and red spectral regions.

Figure SI-4-2 presents the PL experimental results for the 532 nm excitation, by using a 512 - 560 nm filter for detection and avoid the excitation peak. The green part of the leaf presents a broad peak at the red side of the spectrum (675 - 825 nm). The yellow part of the leaf presents two main peaks (orange colour line) between 560 -

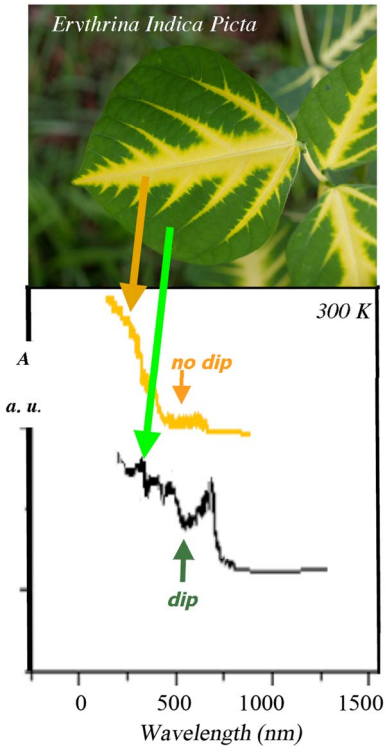

Figure SI-4-1. Represents the absorption x wavelength for a leaf, measured at room temperature. This is the usual behaviour for natural leaves, with a deep within the green surface of the leaf, at the green spectral region. The deep within the green spectral region for green leaves is attributed to chlorophyll no absorption. Note that the yellow part of the leave presents no deep within the green spectral region (535 nm) and chlorophyll is still there. Above 700 nm excitation there is practically no absorption. This figure is to be compared to Figure 8 within the main text. Base line: air, Equipement: Cary 50E.

750 nm. So, the 532 nm excitation gives red shift light emission on both regions.

Figure SI-4-3 presents the leaf excitation by short wavelength (386 nm) light gave green light as emission. As there is no green light excitation for the 386 nm we can come to a controversial question: is the green colour that our eyes see on plants mostly an emission or a reflection? If it is an emission, it is contrary to what we learn in schools and specialized literature [1-3,13,15]. Note that these experiments were performed in vivo and not on chemicals separated from leaves. The conversion mechanism from ultra-violet, violet and blue excitation to green, yellow and red emission is postulated as primarily due to type II energetic interfaces. This proposition does not imply that there is no green (and others colours) reflection, transmission and diffusion (scattering) when leaves are excited with sunlight. Also, it cannot be ruled out the possibility of green absorption and red shift green emission by the many possibilities of existing type II interface within a leaf (see **Figure SI-4-4**). This means

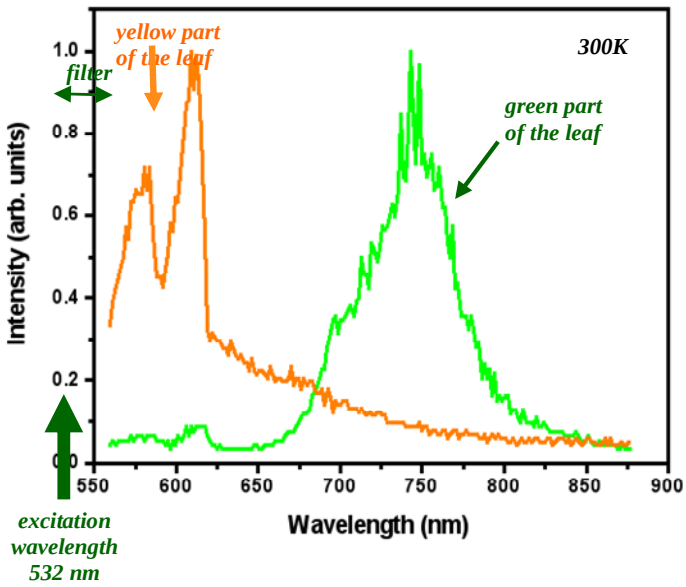

Figure SI-4-2. Room temperature photoluminescence spectra of yellow-green intact *Erytrina indica picta* leaves, excited with 532 nm wavelength, 10 ns pulses from a Nd: YAG laser. To avoid the 532 nm laser line, a 532 - 560 nm filter is placed between the leaf and the spectrometer. Orange spectrum is from the yellow part of the leaf. Green colour spectrum is from the green part of the leaf. No correction is proposed for the intensity axe. No smoothing was performed for both curves. These two spectra suggest that the emission spectrum of different regions (colours) in a leaf depends also on the excitation wavelengths. This result shows clearly that leaves' internal machinery is able to absorb more energetic photons and emit less energetic photons. Both curves show that there is absorption of green light, an internal transformation and emission at longer wavelength (lower energy) by the leaves.

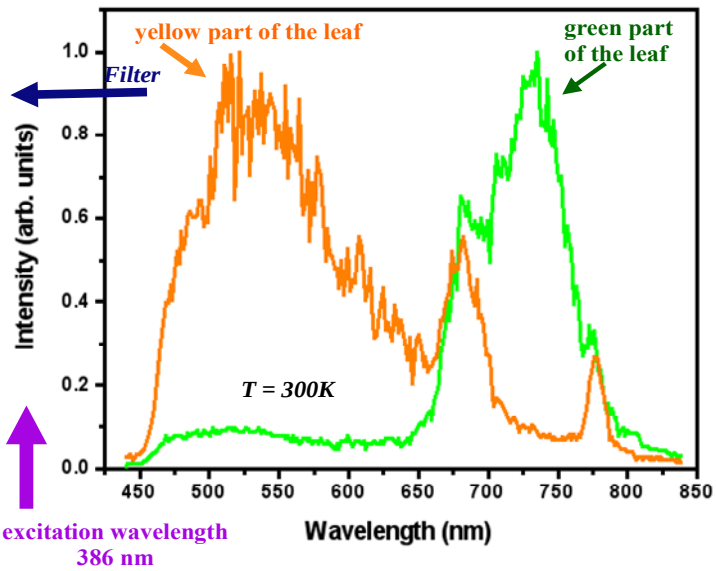

Figure SI-4-3. Room temperature photoluminescence spectra of yellow-green intact *Erytrina indica picta* leaves, excited with 386 nm wavelength, 10 ns pulses from a Nd:YAG laser. To avoid the 386 nm laser line, a cut-off filter below 450 nm is placed between the leaf and the spectrometer. Orange spectrum is from the yellow part of the leaf. Green colour spectrum is from the green part of the leaf. No correction is proposed for the intensity axe. No smoothing was performed for both curves. Note that the yellow part of the leaf has much higher green colour intensity than the green part of the leaf. Also, the green part of the leaf presents a much higher red intensity than the yellow part of the leaf. These two spectra suggest that the emission spectra of different regions (colours) in a leaf depend also on the excitation wavelength. This result shows clearly that leaves' internal machinery is able to absorb more energetic photons and emit less energetic photons. The observed green intensity is an emission and not a reflection, since there is no excitation with green colour. Note that the leaf is absorbing non-green photons and emitting green photons. It means that the green colour of plants is not only composed by green colour reflection.

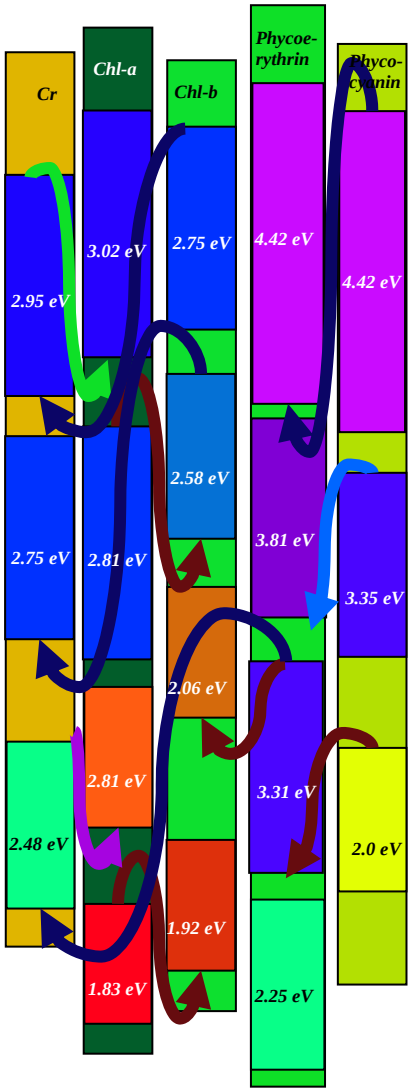

Figure SI-4-4. The Mother Nature puzzle. Representation (on vertical strips) of energy band gap for the leaves' constituent, containing 3 - 4 mains absorption peaks depicted within each strip. Each coloured rectangle with eV energy represents energy peaks absorption for the molecules. These energy bands absorption were taken from the literature [13,15]. They represent possible band gap energies within each individual molecule (separated from leaves). The authors do not know the energy bandgap relative positions for the chromophores in leaves. This means that electrical charges travelling on the leaves' molecules energetic bands should see energetic steps (up or down) that are not known. As the ground state energy energetic representation does not represents any natural and physical entity, to much work is needed to find out these energetic steps for *in vivo* leaves. The energy bands absorption for the cell, protoplast and chloroplast environment are not known by the authors. From one of these band gaps energy relative positions, a staggered one can emerge the main green colour of leaves we have today, for each excitation photon. From others energy relative positions emerge the others less intense colours as yellow, brown, red, from leaves. Genetically leaves can use them on machinery for adaptation/evolution and have different colours as emissions. Note also that these energy absorption values were taken from chemical separated from the leaves. For leaves "*in vivo*", it should change these values because the emission and absorption properties are also interface related. Note that these strips configuration is only one in between many others possibilities to have type II (staggered), type I and type III energetic interfaces (see text). The arrows indicate possible staggered energy band gap relative position and (e–, h+) recombination/transitions. This figure shows that, even for a non *in vivo* situation, it is impossible not to have a staggered band gap energy configuration between two or more molecules. The size of molecules and distances in between molecules within a leaf is about 1 nm. As discussed within the text, the electrical charges wavefunction penetration is much higher that 1 nm. The involved attraction/recombination/emission mechanism cannot be considered as a non quantum mechanics one. The staggered energy configuration gives us the physical situation to have a quantum mechanism for photosynthesis. As (e–, h+) are seated on different materials, quantum k selections rules do not hold anymore for these recombination/transitions/ emissions when considering type II energetic interface. eV represents the electron volts energy from the absorption energy peaks, extracted from the literature. Cr = carotene, Chl = chlorophyll.

interface absorption, as discussed in the main text.

Blue-green laser induced fluorescence from intact leaves has been observed by many research groups, using UV (308 nm) excitation, as M. Broglia and E. Chapelle *et al*. [39,40]. There is no conclusion presented by these authors, for the observed green fluorescence. Their results show also that the blue-green-red fluorescence can be ascribed to others structures, such as cell envelopes and vacuolar solutes [39,40]. This indicates that the environment of the constituents of the leaves play an important role in colour emission from leaves. Nanosecond decay of chlorophyll fluorescence from leaves has been attributed to the recombination of separated charges in the reaction centre of PSII [30]. The environment of the leaves' constituents and the recombination of separated charges, both support our proposition for green light emission as being mostly a type II interface mechanism (see text).

Figures SI-4-2 and **3** show that leaves' constituents, composed of organic materials, are able, with their internal machinery to transform absorbed photons on to emitted photons of lower energy. We propose that many of these mechanisms can be associated to type II interface emission. Some of them can be associated to absorption and emission at nearly the same wavelength (interface absorption/recombination/emission).

As most of the leaves contain many kinds of molecules having 3 - 5 absorption peaks, when separated from the matrix, it is reasonable to expect many possible density of states energy band overlap from these absorption bands when they are not separated from the leaf (using intact leaves).

On **Figure SI-4-4** we present one of these type II interfaces possibilities for many chemicals green leaves constituents. This figure shows that it is impossible not to have type II interface energetic configuration between the leaves' constituents.

Comparing Staggered Energy Band Gaps and the Presently Accepted Ground State Energy Model

The currently accepted model for the photosynthesis mechanism is based roughly on absorption of visible sunlight in the red and blue regions of the spectra, with no absorption (and consequently a conclusion to the existence of a reflection and/or scattering mechanism) in the green spectral region [1-3,13,39-42]. The currently accepted model for photosynthesis is based on classical physics and uses the ground state energy (GSE) configuration to explain the light absorption by certain molecules and its energy transfer to others molecules (FRET). As indicated within the text, the accepted model suffers from few problems concerning the charges separation and violations of physical laws.

Contrary to usual believes, the absorption of photons is not enough to have electrical charges separated [1,13, 80]. The absorption of photons gives rise to an excited state between e– and h+, called exciton. To break up this excitonic energetic configuration we need a physical energetic configuration to allow a driving force to perform this work. This driving force should come from a varying potential (the origin of the electric field). Without an appropriate electric field and without spending energy to separate e– from h+ any other model violates physical laws.

The present proposed model for photosynthesis, based on type II energetic interfaces, is based on the sun visible light spectra absorption by the Nature's green leaves constituent. These materials can be chlorophylls, carotenoids, phycoerythrin, phycocyanin, protoplast, water, etc and the physical structure within a chloroplast. The type II energetic configuration and its application to explain electrical charges separation possess all the physical tools (energetic configuration, electric field and spent energy) to separate e– from h+.

The green (or yellow or red) colours of Nature's leaves depend on the (e–, h+) wavefunction overlap or tunnelling process. It is a very fast process (compared with usual CB-VB semiconductor recombination mecha- nism) and its efficiency comes from the non existing quantum mechanics selection rules, even if it is a quantum mechanics assisted mechanism as proposed within the main text.

Recently many papers based on very sophisticated and beautiful optical experiments got to the proposition that photosynthesis is a quantum mechanical mechanism, but without presenting it [64-71]. The present staggered, type II interface, band gap energy proposal supports this quantum mechanical dynamic mechanism. Based on theoretical calculations, De Angelis *et al*. got to the conclusion for a staggered energy representation between two organic molecules, the same concept holds for inorganic/ organic materials [11,47-60]. That is exactly what we are proposing: (e–, h+) charges have energetic steps when travelling from a material to another. This physical energetic steps concept cannot be put beside and it is the basis for when working and considering different materials. In another way, electric charges have always energetic steps when moving from a material to another. On the contrary, the ground state energy representation (or a band gap engineering, old of tens of years) is an unrealistic and a non-existing physical interface energetic representation [1-5,7-13]. The ground state energy does not allow a quantum mechanics mechanism development for the photosynthesis first step explanation [4-10]. There is no proof of and for the "ground state energy" (GSE) representation. Charges do not care about GSE representation. Charges care about energetic steps within the molecules

or in between the molecules (or materials). GSE representation does not allow the apparition of an electric field for both (e–, h+) charges separation. GSE representation does not allow the apparition of the spent energy to separate electrical charges under attraction. In this sense, the GSE representation violates physical laws in trying to explain the charges separation mechanism; the photosynthesis first step process. Leaves have their internal machinery, able to absorb photons and emit light at lower energy, to waste quickly (emission) most of the visible sunlight radiation. The ~79% absorption (see text) of visible light by leaves should follow the staggered energetic representation to get rid of most of the absorbed visible (400 - 700 nm) light [13-72].

