Porphyrinoid–Fullerene Hybrids as Candidates in Artificial Photosynthetic Schemes

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Abstract: Natural photosynthesis inspired the scientific community to design and synthesize molecular assemblies that possess advanced light-harvesting and electron-transfer features. In this review, we present the preparation and the photophysical investigation of novel porphyrin–fullerene hybrids acting as artificial photosynthetic systems. Porphyrinoids stand as chlorophyll analogues and have emerged as suitable photosensitizers in supramolecular electron donor–acceptor hybrids. Fullerenes (C_{60}) are versatile electron acceptors with small reorganization energy and low reduction potentials. The novel derivatives presented herein mimic the fundamental features of the photosynthetic reaction center, namely, light harvesting, charge separation, and charge transport. To this end, a comprehensive analysis on these key processes that occur in various porphyrin–fullerene entities is illustrated in this work.

Keywords: fullerene; C_{60}; porphyrin; artificial photosynthesis; electron transfer; energy transfer

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1. Introduction

The primary process in natural photosynthesis is the collection and subsequently the conversion of sunlight into chemical energy [1]. To achieve this conversion, sequential photo-induced energy transfers are required, which are followed by an electron transfer process in the reaction center [2]. The photosynthetic reaction center of photosystem II consists of a protein scaffold that contains porphyrinoids in a self-assembled structure [3]. This porphyrinoid-based scaffold is the light harvesting antenna system which absorbs sunlight and efficiently transfers it to the reaction center. Natural systems have motivated researchers to develop artificial photosynthetic systems that mimic the basic processes of photosynthesis in order to achieve solar energy conversion into valuable fuel products and electricity [4,5].

In an ideal artificial photosynthetic scheme, a light harvesting dye absorbs solar irradiation and, upon its excitation, transfers the energy to another dye—the so-called photosensitizer. Subsequently, an electron transfer process occurs between the photosensitizer and an electron acceptor, forming a charge-separated state [1]. Throughout the last few decades, the research community has developed simple artificial photosynthetic schemes in order to comprehend all the important processes that govern natural photosynthesis [2]. In such systems, the electron and/or energy transfer processes between all components that comprise the artificial scheme were studied extensively. Notably, the majority of such artificial photosynthetic systems in the literature are based on porphyrinoids and fullerene derivatives [6,7].

Porphyrinoids, are extremely versatile materials from a synthetic point of view [8] and thus have been widely utilized in various chemistry fields, such as opto-electronics [9], catalysis [10,11], electrochemistry [12,13], etc. Due to their unique characteristics, namely, strong absorption features, great photo- and thermal stability, and most importantly, tunable electro-hemical and photophysical properties [14], are the ideal photosensitizers in artificial schemes [15]. Thus, tailoring the physical and the chemical characteristics of porphyrin derivatives stimulated their broad use in applications such as artificial photosynthesis and solar energy conversion [5,16]. The most frequently studied systems consist of porphyrin derivatives coupled with an energy donor and/or an electron acceptor moiety. Chromophores such as boron–dipyrromethenes (BODIPYs) or ferrocenes have been widely used as energy donors, while the most commonly tested electron acceptors are fullerenes, carbon nanotubes, and naphthalene diimides [17].

Undoubtedly, the most broadly investigated electron acceptors in artificial schemes are fullerenes and particularly C_{60}, since these carbon-based materials retain distinctive electronic and photophysical features. More specifically, their rigid structure permits the stabilization of charged moieties through the delocalization of electrons or holes. Furthermore, fullerenes and their carbon-based derivatives exhibit rich electrochemical behavior, namely, six equally spaced reversible reductions can be detected in their cyclic voltammograms [18]. Last but not least, fullerenes can diminish the charge recombination processes, due to their small reorganization energy, promoting an increased lifetime of the ion pair.

There are two main methods to connect chromophores with electron acceptors: i) the covalent approach in which the moieties are linked together through a rigid bond and ii) the noncovalent connection of entities via supramolecular interactions (dipoles, hydrogen bonds, π–π interactions, and metal–ligand axial coordination) [6]. In general, the covalently linked donor–acceptor assemblies present increased lifetime of the charge-separated state compared to the supramolecular systems. To date, the most efficient artificial photosynthetic scheme, in terms of intramolecular charge transfer, is a covalently linked ferrocene–porphyrin–fullerene hybrid described by Imahori et al. [19]. More specifically, the reported triad displayed a lifetime of the charge-separated state of 0.38 seconds, a value comparable to that observed for the bacterial photosynthetic reaction center [19].

In this perspective review article, we illustrate examples of porphyrinoid–fullerene conjugates reported in the literature from our and other research groups, noting all significant findings concerning the field of artificial photosynthesis. In the first part (2.1), we present covalent and noncovalent connected porphyrinoid–fullerene derivatives that were synthesized using porphyrin, corrole, and phthalocyanine chromophores. In part 2.2, we illustrate how the distance between zinc metallated porphyrinoids and C_{60} affects the electron transfer process and the charge recombination. In the last part of this article (2.3), we demonstrate that the increasing number of metal–ligand coordination bonds between the porphyrins and the C_{60} derivatives can positively influence all the above mentioned processes.

2. Porphyrinoids Connected with Fullerenes

2.1. Covalent and Noncovalent Connected Porphyrinoid–Fullerene Assemblies

Numerous covalent and noncovalent connected systems based on porphyrinoids and carbon allotropes (fullerene C_{60}, graphene, and nanotube) have been prepared and tested as donor–acceptor (D–A) hybrids that mimic photosynthesis [20]. In the majority of these works, the photophysical events were comprehensively examined, revealing the presence of subsequent energy and electron transfer processes [15,21]. Our research group has published plenty of covalent and noncovalent connected porphyrinoid–fullerene assemblies over the last few years. Specifically, porphyrins, phthalocyanines, and corroles have been attached onto appropriate functionalized fullerene moieties, hence exploring different synthetic approaches.

In such multichromophore assemblies, the nature of the spacer that connects the electron donor moiety (e.g., porphyrin) with the electron acceptor (e.g., C_{60}) is of great importance. To be more

specific, the linkages between the entities can definitely influence both the dynamics and the kinetics of photo-induced electron transfer process (PET) [22,23]. To identify the effect of the different connection to the photophysical properties; conjugated, nonconjugated, flexible, and rigid bridges were utilized in plenty artificial photosynthetic systems containing porphyrinoids and fullerenes [24,25].

To that end, we synthesized a series of covalently linked porphyrin–C_{60} dyads in order to investigate the impact of a rigid bridge between the porphyrin macrocycle and the C_{60} moiety [26]. More specifically, we studied whether the insertion of a spacer would affect the electron transfer process and consequently the photophysical properties of the dyads. The rigid bridge that we introduced was a triazole ring derived from an azide–alkyne Huisgen cycloaddition [27] between azide–porphyrin and 4-ethynylbenzaldehyde. In general, Huisgen cycloaddition has been proven a very efficient way to link porphyrins with other chromophores under mild conditions, offering high reaction yields [28]. In our case also, the porphyrin–C_{60} dyads were produced in high yields, performing a Huisgen cycloaddition followed by a Prato reaction with fullerene C_{60}. Transient absorption spectroscopy studies demonstrated that upon photo-excitation of the porphyrin, a charge-separated state $(ZnP)^{+}-(C_{60})^{-}$ is formed in all dyads. The dyad in which the triazole spacer was inserted between the porphyrin and the fullerene (C_{60}–*tr*–ZnPCOOH, Figure 1) presented the most long-lived lifetime of the charge-separated state, namely, 1260 ps in benzonitrile. These findings suggested that the presence of the triazole bridge enhances the electronic communication in such dyads and more importantly improves the photovoltaic parameters of the solar device, since those dyads were utilized as sensitizers in photovoltaic devices.

Aromatic triazoles have been widely utilized in the literature as linkers in order to covalently connect chromophores together [29]. Furthermore, the triazole bridge has been proved as an effective π-conjugated bridge that assists intramolecular electron transfer processes in multichromophore systems comprising porphyrin entities [28]. In 2011, de Miguel et al. published a series of triazole-linked porphyrin–fullerene dyads examining the influence of the connectivity at the triazole spacer to the electron transfer dynamics [30]. From all reported porphyrin–fullerene dyads, p1p–ZnP–Tri–C_{60} (Figure 1) demonstrated the best performance in terms of lifetime of the charge-separated state. To be more specific, the lifetime of the charge-separated state of p1p–ZnP–Tri–C_{60} was 646 ns in benzonitrile, indicating that the *para–para* connection between the donor and acceptor moieties is the optimum.

In another example, our research group replaced the porphyrin chromophore with a corrole derivative and prepared the first corrole–azafullerene dyad (corrole–$C_{59}N$), studying the electrochemical and photophysical features of this entity (Figure 1) [31]. In order to synthesize this fullerene–corrole dyad, an amide coupling reaction was performed between an amino-substituted corrole and an azafullerene–acid. The photophysical investigation of corrole–$C_{59}N$ revealed that the corrole based fluorescence is strongly quenched by the presence of the azafullerene entity, indicating an efficient electronic communication between the two components in the excited state. The femtosecond transient absorption spectroscopy studies shed light into this assumption by identifying the formation of the $(corrole)^{+}-(C_{59}N)^{-}$ charge-separated state. The lifetime of this charge-separated state corrole–$C_{59}N$ was 1021 ps in o-xylene, which was relatively lower than that of the C_{60}–*tr*–ZnPCOOH derivative (1260 ps). Nonetheless, the corrole–$C_{59}N$ dyad could be a potential candidate as an artificial photosynthetic system and could be utilized in solar conversion applications.

D'Souza et al. reported the first covalently linked corrole–fullerene dyad which was studied as a mimic model of the photosynthetic reaction center consisting of the fullerene C_{60} as an electron acceptor and the free base corrole as an electron donor [32]. In this work, the corrole–C_{60} (Figure 1) dyad yielded higher lifetimes of the charge separation state compared to similar porphyrin analogues. More specifically, the best observed lifetime of the radical ion pair was 6300 ns using cyclohexane as solvent, while in THF, a significantly shorter lifetime was calculated (38 ps). Consequently, the charge recombination rates are highly dependent on the solvent polarity in such corrole–fullerene dyads in contrast to the porphyrin–fullerene analogues.
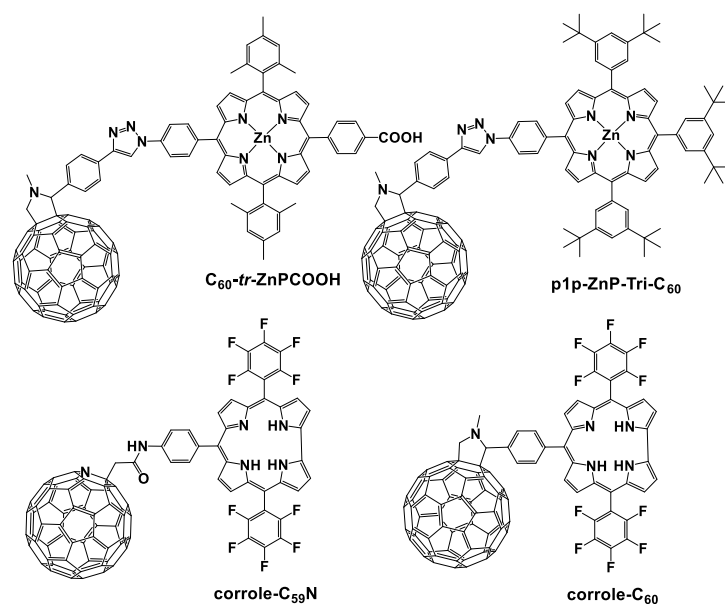
Figure 1. The covalent linked C_{60}–*tr*–ZnPCOOH, p1p–ZnP–Tri–C_{60}, corrole–C_{59}N, and corrole–C_{60}.

We have also examined the noncovalent approach via connecting zinc–porphyrins and zinc–phthalocyanines with pyridyl-modified C_{60} moieties. As illustrated in Figure 2, we synthesized a zinc–porphyrin–C_{60} derivative (C_{60}–pyr·ZnP) that was formed by metal–ligand coordination between the zinc center of the porphyrin ring and the pyridyl group of the functionalized fullerene [33]. We comprehensively evaluated the photophysical characteristics of this dyad which exhibited charge separation lifetimes of 25 and 37 ps in anisole and chlorobenzene, respectively. Moreover, C_{60}–pyr·ZnP displayed a radical ion pair state that decayed with lifetimes of 1189 ps in anisole and 991 ps in chlorobenzene. In the same manner, only recently, we prepared an analogous phthalocyanine–C_{60} conjugate [34] (Figure 2). In this study, the C_{60}–pyr·ZnPc hybrid presented a binding constant of 1.3×10^5 M^{-1} in chlorobenzene and 3.6×10^4 M^{-1} in anisole. It is worth noting that this binding constant was greater compared to that of the C_{60}–pyr·ZnP dyad. In addition, the lifetime of the charge recombination process of the $ZnPc^{\bullet+}$–$C_{60}^{\bullet-}$ ion pair state was calculated at approximately 400 ps in chlorobenzene and anisole. Interestingly, these values are in the same order of magnitude with a similar covalently linked ZnPc–C_{60} assembly ($\tau \approx 3$ ns) that has been reported in literature [35].

Ito, D'Souza, and coworkers in 2002 synthesized a series of porphyrin–fullerene conjugates in which modified fullerenes, bearing either pyridine or imidazole, were incorporated as electron acceptors [36]. The photophysical investigation of the porphyrin–fullerene dyad connected through an imidazole linker (C_{60}–Im·ZnP, Figure 2) revealed that the binding constant of C_{60}–Im·ZnP was greater compared to the pyridine analogue. Concerning the transient absorption measurements, upon employment of a noncoordinating solvent such as *o*-dichlorobenzene, an electron transfer process takes place from the singlet excited state of the porphyrin to the fullerene entity. However, when benzonitrile was used as a coordinating solvent, intermolecular electron transfer from the triplet excited state of the porphyrin to the fullerene was clearly detected. The same research groups, one year later, prepared and fully characterized a phthalocyanine–fullerene dyad connected through an imidazole bridge (C_{60}–Im·ZnPc, Figure 2) [37]. Transient absorption experiments showed the successful formation of the radical ion pair $[(C_{60})^-$–Im·$(ZnPc)^+]$ between the electron donating phthalocyanine and the electron accepting fullerene. The charge separation rate of C_{60}–Im·ZnPc was calculated in toluene and *o*-dichlorobenzene and found 1.4×10^{10} s^{-1} and 8.9×10^9 s^{-1}, respectively. In benzonitrile, C_{60}–Im·ZnPc undergoes an intermolecular electron transfer from the excited triplet state of the zinc–phthalocyanine to the fullerene similar to the C_{60}–Im·ZnP.

Taking another step forward, we prepared a supramolecular complex consisting of porphyrin, phthalocyanine, and fullerene in order to investigate this compound as an artificial photosynthetic center mimic [38]. Hence, we synthesized a novel zinc phthalocyanine–zinc porphyrin dyad in which the two chromophores were linked through a pyrazine ring. As shown in Figure 2, the zinc centers of both chromophores were connected with an imidazole substituted fullerene forming C_{60}–Im:ZnPc–ZnP:Im–C_{60}. Following this approach, we were able to prepare a supramolecular D–A entity and analyze the electronic interactions occurring in this system. The investigation of the photophysical studies exposed that there is a strong electronic interaction between the two zinc–metallated porphyrinoids. More specifically, the transient absorption studies indicated that upon photoexcitation of the zinc–porphyrin derivative (ZnP) in the supramolecular complex C_{60}–Im:ZnPc–ZnP:Im–C_{60}, a very efficient energy transfer from the poprhyrin to the phthalocyanine takes place. Subsequently, the excited zinc–phthalocyanine is formed (^{1}ZnPc*), which performs an electron transfer to the fullerene moiety. Thus, we observe the formation of a long-lived charge-separated state between the zinc–phthalocyanine and the fullerene $(C_{60}Im)^-$–$(ZnPc)^+$–ZnP:ImC_{60} with a lifetime of 200 ns, signifying the importance of such complexes in solar harvesting applications. It is worth mentioning that in a recent publication, we synthesized the nonmetallated porphyrin analogue of this supramolecular compound [39]. As expected, in this supramolecular complex, the respective sequential energy and electron transfer events take place as well. However, due to the absence of the second fullerene moiety axially coordinated to the porphyrin moiety in this complex, the photophysical investigation is much more controllable.
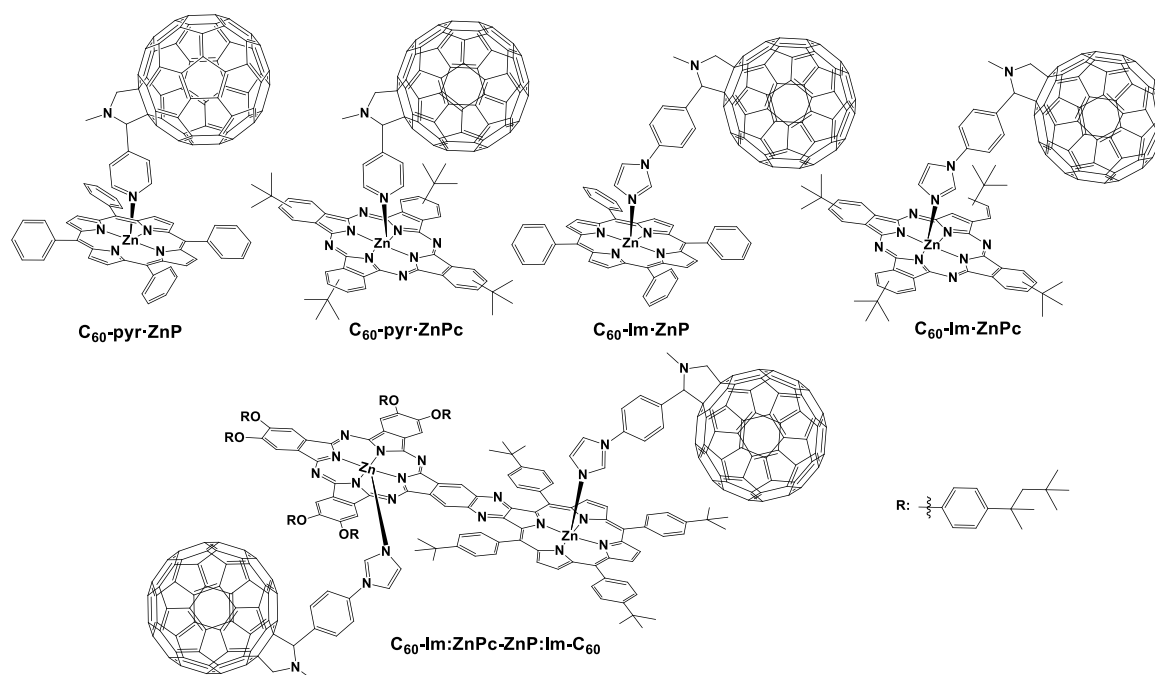
Figure 2. The chemical structures of the noncovalent linked porphyrinoid–fullerene compounds. C_{60}–pyr·ZnP, C_{60}–pyr·ZnPc, C_{60}–Im·ZnP, C_{60}–Im·ZnPc, and C_{60}–Im:ZnPc–ZnP:Im–C_{60}.

2.2. The Influence of the Distance Between Porphyrinoids and C_{60}

There are plenty of covalently linked porphyrinoid–fullerene hybrids reported in the literature in which the thorough investigation of their photophysical properties and electronic features was performed [15–17,21,22]. What is more, Segura et al. in 2005 reported that increasing the distance between the electron donor and electron acceptor components by introducing a conjugated bridge leads to increased lifetime of the charge separation state [40]. Our group, in an effort to determine whether the length of a rigid bridge affects the electronic communication in a noncovalent porphyhrin–fullerene

dyad, synthesized C_{60} moieties using oligo(*p*-phenylenevinylene) (oPPVs) bridges of different sizes [33]. Hence, we synthesized fullerene entities connected with oPPVs of different lengths bearing pyridyl groups. The pyridyl groups of the formed C_{60}–oPPV–pyr moieties are well-known nitrogen ligands which enable the formation of metal–ligand coordination bonds with zinc–porphyrin chromophores. In Figure 3, the chemical structures of the three different porphyrin–fullerene dyads are presented. We synthesized a porphyrin–fullerene dyad in which the C_{60} entity is directly coordinated onto the zinc of the porphyrin ring through the pyridyl group abbreviated as C_{60}–pyr·ZnP and two new dyads with one or three extra phenylenevinylene groups, C_{60}–PPV1–pyr·ZnP and C_{60}–PPV3–pyr·ZnP, respectively.
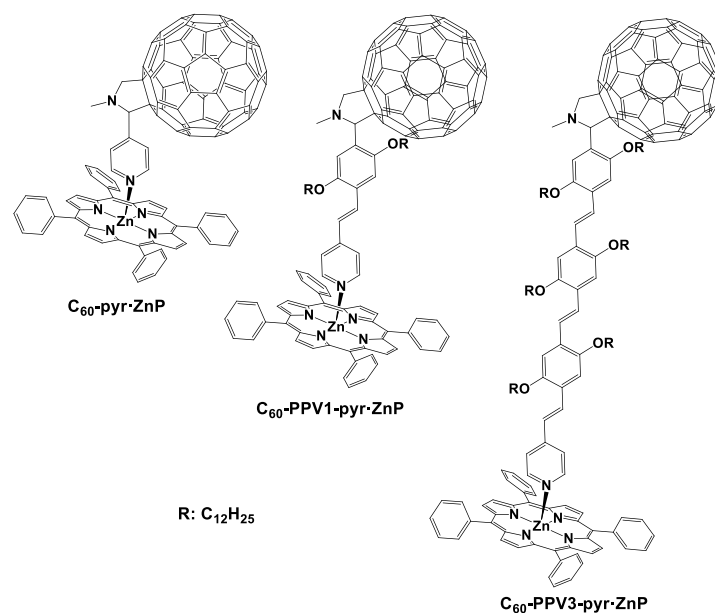
Figure 3. The noncovalent porphyrin–fullerene dyads C_{60}–pyr·ZnP, C_{60}–PPV1–pyr·ZnP, and C_{60}–PPV3–pyr·ZnP.

In the ground state, there is not any noticeable electronic interaction between porphyrin and C_{60}. Nevertheless, the fluorescence experiments conducted in all three dyads implied that in the excited state, there is a very efficient energy or electron transfer between the zinc–porphyrin and the fullerene. We performed transient absorption measurements that confirmed the above hypothesis—namely, the formation of the reduced C_{60} (radical anion) and the oxidized zinc–porphyrin (radical cation) were observed. Interestingly, in the case of C_{60}–PPV3–pyr·ZnP, there was a faster charge recombination process despite the greater distance between the porphyrin and the fullerene. This is in contrast with the tendency reported for the covalently linked porphyrin–fullerene entities, since in those cases, increasing the distance leads to higher charge separation lifetimes [40]. In those cases, the different distance between the electron donor and electron acceptor components does not affect the reorganization energy of the system [33,40]. By contrast, in our case, C_{60}–PPV1–pyr·ZnP and C_{60}–PPV3–pyr·ZnP demonstrated reorganization energies of 0.74 and 0.91 eV, respectively. In addition, the theoretical calculations that were performed showed that the pyridinic nitrogen disrupts the electronic pathway from the zinc–porphyrin to the fullerene. All the above observations highlight the importance of controlling the reorganization energy in noncovalent supramolecular assemblies and thus modulate the desired properties of such schemes in the field of energy conversion based on artificial photosynthetic mimics.

In a similar manner, we also examined to what extent the distance between the donor and the acceptor entities affects their electronic communication in phthalocyanine–C_{60} assemblies. Once more, we achieved that by inserting varied lengths of oligo(*p*-phenylenevinylene) bridges between the zinc–phtalocyanine and the fullerene (C_{60}–pyr·ZnPc, C_{60}–PPV$_1$-pyr·ZnPc, and C_{60}–PPV$_3$-pyr·ZnPc, Figure 4). Accordingly, in this case, a dependence was observed between the increasing distance of the

donor–acceptor moieties in the three studied assemblies (from 8.8 to 29.1 Å), and charge-separated state lifetime was increased from 0.4 to 86.6 ns, and reorganization energy was also amplified from 0.43 to 0.63 eV.

Plenty of research groups have dealt with the preparation and photophysical investigation of similar phthalocyanine–fullerene entities over the years [22,23]. As illustrated in Figure 4, Göransson et al. synthesized a phthalocyanine–fullerene dyad linked through an oligophenylene–ethynylene bridge [41]. This kind of connection was used as a bridging unit in plenty of research works, promoting the electron transfer over long distances [42–44]. In addition, the ethylene groups between donor and acceptor moieties assist the high rates of electron transfer processes [45,46]. The photophysical investigation of the phthalocyanine–fullerene dyad (ZnPc–OPE–C_{60}) proved that an efficient photo-induced electron transfer occurs between the electron donor zinc–phthalocyanine and the electron acceptor C_{60} forming the radical ion pair [$(ZnPc)^+$–OPE–$(C_{60})^-$] of the dyad. The rate of the electron transfer was 1.1×10^9 s^{-1}, whereas the recombination process was very fast at approximately 5×10^{10} s^{-1}.
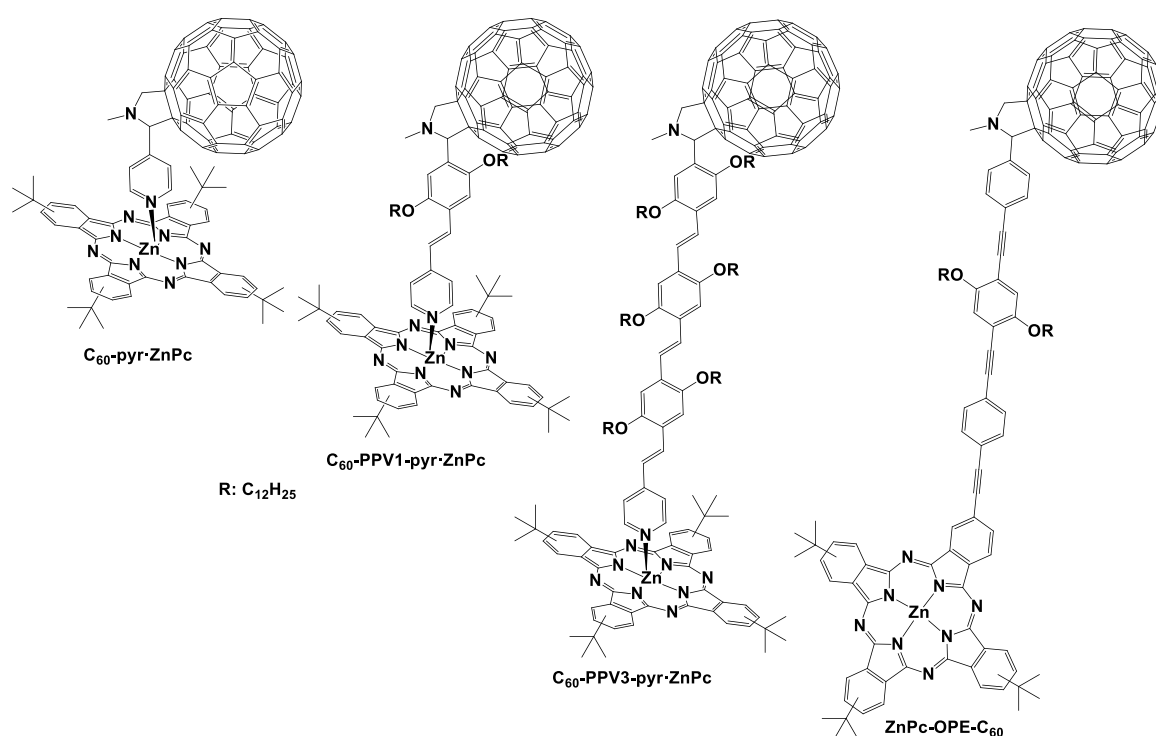
Figure 4. The noncovalent porphyrin–fullerene dyads C_{60}–pyr·ZnPc, C_{60}–PPV1–pyr·ZnPc, C_{60}–PPV3–pyr·ZnPc, and ZnPc–OPE–C_{60}.

2.3. Increasing the Number of Porphyrin Derivatives in Porphyrin–C_{60} Entities

Consequently, we explored the impact of increasing the number of zinc–porphyrins that were linked to fullerene derivatives in supramolecular porphyrin–fullerene conjugates. Accordingly, we synthesized fullerene entities functionalized with two or four pyridyl groups offering binding sites for zinc–porphyrin derivatives. More specifically, fullerenes bearing one or two conjugated bridges which enable the coordination of one or two flexible porphyrin dimers (ZnP$_2$) in order to create the D–A porphyrin–fullerene hybrids C_{60}–dipyr·ZnP$_2$ and C_{60}–tpyr·[(ZnP)$_2$]$_2$, respectively (Figure 5) [47,48]. As illustrated, in both cases, the zinc centers of the ZnP$_2$ are coordinated with the pyridyl groups of the functionalized fullerenes. In these reports, by utilizing increased number of porphyrin chromophores onto a fullerene, we additionally simulated the structure of the photosynthetic reaction center compared to our previously reported C_{60}–PPV–pyr·ZnP derivatives [33]. The supramolecular

hybrids also presented enhanced solubility in solvents with varied polarity such as THF, DCM, Toluene, and o-DCB. This property is significant for potential application in solar harvesting devices.
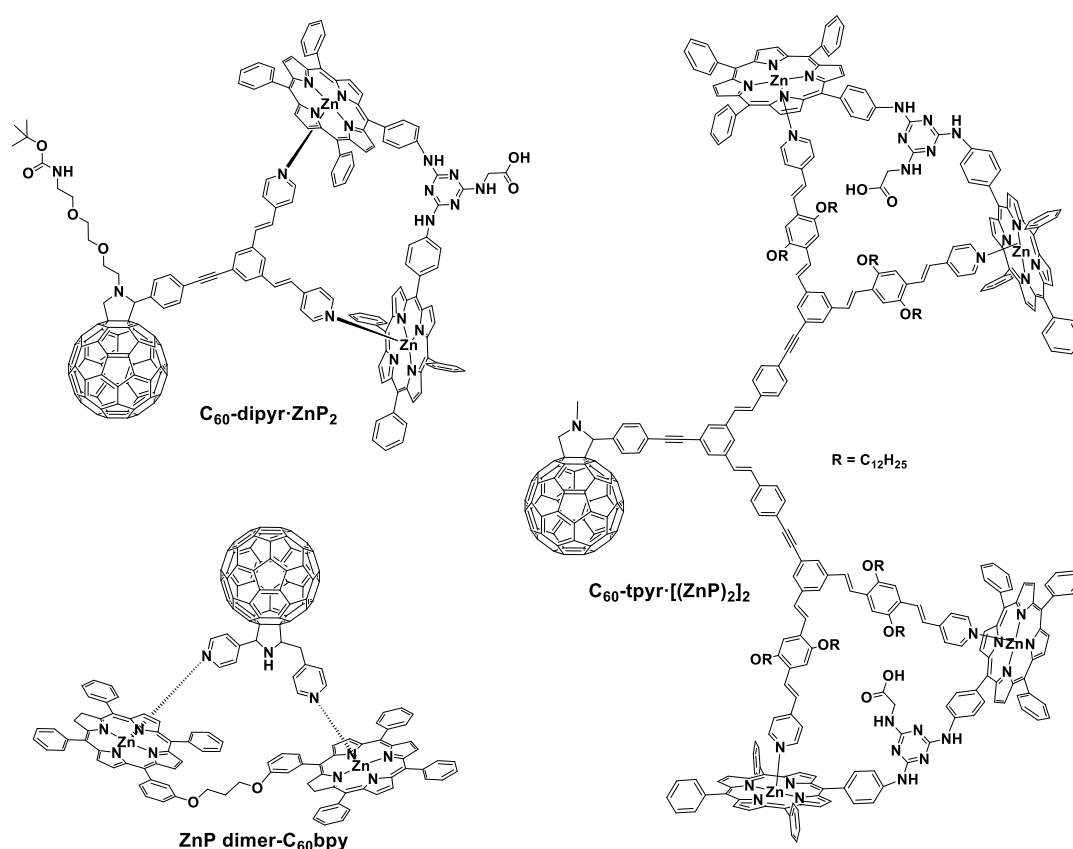
Figure 5. The supramolecular porphyrin–fullerene conjugates C_{60}–dipyr·ZnP_2 and C_{60}–tpyr·$[(ZnP)_2]_2$ and ZnP dimer–C_{60}bpy.

In order to verify the successful formation of both porphyrin–fullerene hybrids (C_{60}–dipyr·ZnP_2 and C_{60}–tpyr·$[(ZnP)_2]_2$), absorption and fluorescence titration experiments were carried out. In either case, the binding constant was greater (5×10^5 M^{-1} in anisole) compared to that of similar systems with more than one coordination binding site [49]. The femtosecond transient absorption studies for C_{60}–dipyr·ZnP_2 and C_{60}–tpyr·$[(ZnP)_2]_2$ showed that upon photo-excitation of the porphyrin entity, an efficient electron transfer process occurs from the first excited singlet state of porphyrin dimer to the fullerene. This leads to the rise of the ZnP_2 radical cation as well as the C_{60} radical anion forming the charge-separated states $(C_{60})^-$–dipyr·$(ZnP_2)^+$ and $(C_{60})^-$–tpyr·$[(ZnP_2)_2]^+$. The lifetime of the charge-separated states, using toluene as solvent, was 1500 ps for C_{60}–dipyr·ZnP_2 and 2400 ps for C_{60}–tpyr·$[(ZnP)_2]_2$. It is worth noting that the formation of these states was very rapid, implying that in both cases, the pyridyl groups promote the charge separation process without shortening the lifetime of the charge-separated state. Overall, we established that increasing the number of porphyrinoids in porphyrin–fullerene hybrids is beneficial for the binding constant, the fast charge separation process, and the increased lifetime of the charge-separated state.

In a previous report, D'Souza et al. also assembled a zinc porphyrin dimer with a fullerene derivative that was functionalized with two pyridine groups [50], similar to our work [47]. The fullerene chromophore was suitably modified with two pyridine groups offering binding sites for the zinc–porphyrin dimer, as illustrated in Figure 5, forming the supramolecular complex ZnP dimer–C_{60}bpy. Steady-state and time resolved fluorescence studies showed that efficient intramolecular photo-induced electron transfer process occurs from the zinc–porphyrin dimer to C_{60}. The nanosecond

transient absorption studies indicated that the charge recombination process was very fast. More precisely, the rate was 2×10^8 s^{-1} using *o*-dichlorobenzene as solvent.

3. Conclusions

In this perspective review article, we presented various covalent and supramolecular artificial photosynthetic schemes that our group have studied over the past decade, analyzing the most important findings of these works. All these D–A systems consist of fullerene derivatives that act as electron acceptors and porphyrinoids, such as corroles, porphyrins, and phthalocyanines, utilized as electron donating units. The thorough photophysical investigation in all systems revealed efficient electronic communication between the donor and acceptor entities. What is more, in all cases, the conducted transient absorption measurements proved the formation of a charge-separated state, which is formed after an electron transfer originating from the singlet excited state of each photosensitizer.

Regarding the covalently linked assemblies, it is clear that their preparation is rather demanding, since multistep reactions are required. In addition to that, these hybrids displayed lifetimes of charge-separated state comparable to those of the noncovalent systems; hence, the metal–ligand axial coordination approach is an advantageous strategy for the construction of such hybrids. Concerning the noncovalent assemblies where electron donor monomers (ZnP and ZnPc) were linked to fullerene derivatives, a longer-lived charge-separated state was calculated for the C_{60}–pyr·ZnP hybrid, whereas the phthalocyanine analogue (C_{60}–pyr·ZnPc) demonstrated a larger binding constant. In an effort to determine whether the length of a rigid bridge affects electronic communication in a noncovalent porphyrin–fullerene dyad, we studied two series of porphyrinoid–C_{60} derivatives with bridges of different sizes containing both ZnP and ZnPc chromophores. Even though the different distance between the electron donor and acceptor units does not affect the reorganization energy of covalently linked systems, a dependence between the increasing distance and both the ion pair lifetime and reorganization energy was observed in the supramolecular systems.

Interestingly, the supramolecular schemes C_{60}–dipyr·ZnP$_2$ and C_{60}–tpyr·[(ZnP)$_2$]$_2$, in which properly functionalized C_{60} derivatives are coordinated to metallated porphyrin dimers, presented binding constants that were over one order of magnitude higher than those reported for porphyrin–fullerene hybrids with a single binding site. In addition, the lifetime of their charge-separated state was greater than that of the respective porphyrin–fullerene hybrid with a single binding site. Finally, out of all the described artificial photosynthetic schemes, those which showed the longer-lived charge-separated state are systems incorporating dimeric sensitizer moieties, namely, C_{60}–Im:ZnPc–ZnP:Im–C_{60} and C_{60}–tpyr·[(ZnP)$_2$]$_2$.

Supramolecular hybrids comprising porphyrinoids and fullerene moieties display plenty of imperative as well as desirable features. Specifically, all of them are molecular systems with reliable stability, thus offering the opportunity of straightforward characterization through widely used spectroscopic methods. In addition, for the synthesis of these complexes, well-known and simple experimental procedures are followed, utilizing low-cost reagents and ease purification methods as well. Lastly, the electron transfer processes that take place in such systems can be identified using transient absorption measurements. However, there are a few drawbacks when this class of hybrids is employed that have not been solved yet by the research community. To be more specific, it is very difficult to scale up the synthesis of such compounds, limiting their application in solar energy devices. Moreover, in all cases, the back electron transfer process from the reduced fullerene moiety to the oxidized porphyrinoid entity occurs, limiting the lifetime of the charge-separated state. Overall, such porphyrinoid–fullerene assemblies can provide beneficial directions towards the successful preparation of efficient D–A hybrids as potential candidates for solar energy conversion schemes.

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