Invited Review

Design and photochemical study of supramolecular donor-acceptor systems assembled via metal-ligand axial coordination

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Abstract

The natural photosynthetic light energy harvesting functional nano-architectures, organized exclusively by non-covalent interactions, have inspired the design of artificial supramolecular donor-acceptor systems held solely by self-assembly methods. Various non-covalent interactions have been employed to design such supramolecular conjugates. The present review highlights recent progress made towards the design and photochemical study of energy-harvesting systems assembled by metal-ligand axial coordination. Due to the remarkable photophysical and photochemical properties of porphyrins and phthalocyanines, and importantly, their ability to form metal-ligand coordination bonds, they have been widely used as sensitizers in the construction of donor-acceptor conjugates of this class. Both fullerene and non-fullerene molecules, functionalized with nitrogenous ligands that are capable of donating a pair of electrons to the central metal atom of tetrapyrrolic macrocycles, have commonly been used as electron acceptors. The significance of endohedral fullerenes and carbon nanotubes in mimicking natural photosynthesis by stabilizing the light induced charge-separated states in supramolecular multicomponent donor-acceptor assemblies held via metal-ligand axial coordination interaction is a burgeoning area of research. Particular attention has also been given to the generation of long-lived charge-separated states, in addition to the design principles and characterization of donor-acceptor systems assembled by metal-ligand axial coordination.

Keywords: Porphyrin; Phthalocyanines; Fullerenes; Endohedral fullerene; Carbon Nanotubes; Photoinduced Electron Transfer; Self-assembly; Excitation transfer; Axial coordination

1. Introduction

The major challenge for the 21st century is the search for carbon free clean energy that is abundant, renewable, and replace the currently used fossil fuel derived energy [1-5]. The main reasons to detest fossil fuels are their limited sources and the production of air polluting carbon containing gases which have displayed adverse effects both in the environment as well as in human health. The non-renewable property of fossil fuels is another main reason to find alternatives. Apparently, harvesting sun energy is the answer for fulfilling the increasing energy demand which is directly proportional to the increasing world population. Annually, about 120,000 TW (1 TW = 10^{12} Watts) of solar energy, which is about 8,000 times the total global energy requirement, hits the Earth's surface. However, the disperse nature of sun light mandates efficient methods of light energy harvesting and techniques to fulfill the necessity of renewable and clean energy demand for the next generation. In this context, the natural photosynthetic process stands out as one of the most prominent and reliable methods to harvest light energy. For millions of years, green plants and some bacteria have been harvesting light energy and converting it into chemical energy to perform their physiological activities. This establishes a grand challenge to the scientific community, at this point, to design and deploy such biomimetic materials to harvest light energy efficiently. Out of various existing and deployable artificial photosynthetic schemes [6-16], this review focuses on the design and study of energy harvesting supramolecular donor-acceptor systems comprising metal-ligand axial coordination.

The first review on photoactive donor-acceptor systems based on metal–ligand axial coordination was published by us in 2005 covering mainly metal tetrapyrrole-fullerene systems [17]. Since then, a few reviews and monographs have appeared in the literature [18-34]. In addition, nanocarbons beyond fullerenes, viz., carbon nanotubes and endohedral fullerenes, have been also employed [35-38]. To keep things in perspective and current, this review highlights work done since 2009. Along with nanocarbons, key examples of other electron acceptors used in building such donor-acceptor are also discussed. As reviewed here, the supramolecular donor-acceptor systems assembled using axial coordination binding motif have

resulted in novel systems exhibiting photoinduced energy and electron transfer events in a controlled fashion.

The following sections in the introduction provide the necessary background for the review topic.

1.1 The natural **photosynthetic process**

Natural photosynthetic process is a series of events where green plants utilize light energy, first, to oxidize water into molecular oxygen and to generate four electrons. In the second step, CO₂ is subsequently reduced into the energetic biomolecules, hydrocarbons and sugars, by utilizing electrons generated in the first step. The process of photosynthesis is multifaceted and is challenging to elucidate all of the individual steps [39-43]. Thanks to impressive advances in X-ray crystallography, it has been possible to solve the structure of membrane proteins involved in photosynthesis. The first crystal structure resolved was that of photosystem II (PSII) from the thermophilic cyanobacteria. This helped to understand the mechanistic details of light harvesting, charge separation, and catalysis events. The primary events occurring in PSII of

Fig. 1. Structure of light harvesting center II (LHCII) showing the excitation energy migration from antennae to reaction center [reproduced with permission from Ref. 44].

aerobic cyanobacteria largely follows in other photosynthetic living organisms. The first step of the process involves gathering sufficient light energy through the light energy harvesting complexes [44]. One single light harvesting complex II (LHCII) consists of around 200 chlorophylls (Chls) and 50 carotenoids (Cars) as shown in Fig. 1. The chlorophylls exclusively collect photons from light and transfer them to the reaction center. The major role of carotenoids during this process is to protect the photosynthetic apparatus from photo-damage [45].

In P_{680} , PSII chlorophylls upon photoexcitation transfer an electron to an acceptor system which is subsequently involved in reducing carbon dioxide. This is the site where the light harvesting, charge separation, charge stabilization, and electron transfer take place. The excited state of the primary donor P_{680} rapidly transfers an electron to ChlD1, pheophytin (PheoD1), and eventually to the first acceptor, plastoquinone A (Q_A), and then to the final acceptor, plastoquinone B (Q_B), to stabilize the charge-separated states. After protonation, the acceptor, plastoquinone B (Q_B) forms plastoquinol, $QH_2(B)$, and releases from PS(II) into the matrix which mediates the electron transfer between PSI and PSII. The oxidized form of P_{680}^{+} which acts as a strong oxidant now gets an electron from a Mn_4Ca -cluster in the oxygen evolving complex (OEC). After the abstraction of four consecutive electrons from OEC, two molecules of water get oxidized to generate one molecule of O_2 and four protons. The structure of OEC has been determined by X-ray crystallography and consists of four manganese and one calcium atom which are held together by μ -oxo and hydroxy ligands in a cubane like arrangement. The mechanism behind the oxidation of water by OEC, which is triggered by absorbed light energy, has been extensively studied, and found that the OEC cycle undergoes five oxidation cycles denoted by S_0 , S_1 .. S_4 in the Kok cycle. The S_0 state is the most reduced state, also known as the resting state of the OEC catalyst, whereas the S_4 state is the most oxidized state. Molecular oxygen gets liberated during the process of $S_0 - S_4$ conversion of OEC catalyst [45].

1.2 Artificial photosynthesis

The role of natural photosynthesis is to convert sunlight into other forms of energy and store it in the form of carbohydrates and lipids in green plants. The artificial photosynthetic

process inspired from nature is a technique where sunlight is converted into another forms of energy, viz., electricity and fuels. In principle, a typical artificial photosynthetic system must be comprised of the following components: an antenna which is basically a collection of chromophores that absorb sunlight efficiently throughout the solar spectrum and transfer that energy to another component called the reaction center. The reaction center is where the absorbed excitation energy drives efficient photoinduced electron transfer to an electron acceptor to generate charge-separated states. Thus, a reaction center can be considered a nanoscale photovoltaic device. Additionally, the reaction center could be coupled to a water oxidation catalyst and a proton reduction catalyst for water-to-hydrogen conversion, [or schemes](#) of similar nature [46-48].

1.3 Photoinduced energy and electron transfer processes

One of the most interesting events that occur in nature, particularly in green plants, is the conversion of light energy into chemical energy through photoinduced energy/electron transfer processes after light absorption. The photosynthetic reaction center consists of arrays of porphyrinoids and carotenoids in a self-assembled protein scaffolds to harvest light efficiently. Better efficiencies arise because of the precise nano-architecture which facilitate the intermolecular interactions between the entities [49-55].

Consequently, study of photoinduced energy and electron transfer processes in synthetic donor-acceptor systems becomes of paramount importance. Some of the factors that affect the efficiencies of the light driven processes include nature of molecules (including sensitizers), geometry and orientation of the conjugates, redox potentials, and absorption and emission properties of participating components. Self-assembly and self-organization are the main challenges when designing efficient and robust photonic devices in the laboratory.

Fig. 2 shows the schematic mechanism for photoinduced electron and energy transfer processes. The horizontal lines represent the orbital populated by electrons (shown by arrows). During the process, an electron from excited state chromophore is transferred to the LUMO of acceptor creating a charge-separated state. The radical cation is formed by one-electron oxidation of the donor while the radical anion is formed by one-electron reduction of the

acceptor, which has been experimentally confirmed by various spectroscopic techniques. The process of light induced electron transfer has been first interpreted by the classical electron transfer theory developed by Marcus. Marcus explained the thermodynamic feasibility of both forward and reverse electron transfer in donor-acceptor systems and described the factors affecting the charge separation and recombination processes [56-58].

Fig. 2. Schematic representation of (a) excitation of the chromophore, (b) electron transfer, and (c) energy transfer quenching of the chromophore excited state.

1.4 Single vs multistep electron and energy transfer processes

For ideal photosynthetic model systems, the demanding parameter for electron transfer process between donor and acceptor are fast charge separation and relatively slow charge recombination. A vast number of donor-acceptor systems have been built and studied to achieve long-lived charge-separated states. The photoinduced single-step electron transfer can be achieved by designing simple donor-acceptor (D-A) pairs connected covalently or non-covalently. Here, D acts as a chromophore to capture light and act as a primary electron donor

that transfers an electron to the acceptor (charge separation process, CS) as shown in Fig. 3a. Because of the closeness between donor and acceptor, radical ion-pair formed upon photoexcitation recombines rapidly to its initial ground state (charge recombination process, CR).

To overcome this, multi-modular systems have been designed to generate long-lived charge-separated states. To observe multistep electron transfer, at least three species are required, viz., Donor₂-Donor(D)-Acceptor(A), or Donor(D)-Acceptor(A)-Acceptor(A₂) where D and D₂ are primary and secondary electron donors, and A and A₂ are primary and secondary electron acceptors, respectively [59]. Facile oxidation of D₂ over D, and facile reduction of A₂ over A are a requirement in the molecular design. The photochemical events upon D excitation in D₂-D-A is shown in Fig. 3b. The primary CS product, D₂-D⁺-A⁻ would undergo the thermodynamically feasible hole shift (HS) involving D₂ and D to yield D₂⁺-D-A⁻ charge-separated state. Because of the increased distance between donor-acceptor moieties in the final charge-separated state, longer lifetime of this state can be achieved [60]. A similar photochemical

Fig. 3. Schematic diagram for (a) single-step, (b) multistep electron transfer, and (c) energy transfer coupled with electron transfer processes.

process could be envisioned in the case of D-A-A₂ triad, here, the primary electron transfer product, D⁺-A⁻-A₂ would undergo an electron migration (EM) to yield the D⁺-A-A₂⁻ charge-separated state. Because of the distal separation between the radical cation and anion species, a long-lived charge-separated state can be achieved.

One of the issues with organic sensitizers is their narrow absorption and emission peaks that restrict full utilization of useful solar light in promoting electron transfer [61-62]. This could be overcome by linking suitable antenna entities to the donor site, as shown in **Fig. 3c**. Here, an antenna entity, E having complimentary absorption and emission to D, is directly attached to D. Selective excitation of E would promote excitation transfer to D, either by Förster or Dexter type mechanisms [63]. Excited D could trigger the photochemical events to finally yield D₂⁺-D-A⁻ charge-separated state of appreciable lifetime. It may be noted here that since E and D have different absorption bands, direct excitation of the D is also possible to achieve the D₂⁺-D-A⁻ charge-separated state. The multi-modular system shown in **Fig. 3c** would be an ideal approach due to its maximum utilization of solar light and generation of long-lived charge-separated states. However, as discussed in this review, only a handful of systems are built using self-assembly methods to reveal such multi-step energy and electron transfer events.

Fig. 4. Simplified scheme showing light-to-fuel production using an 'antenna-reaction center' system. WOC = water oxidation catalyst and PRC = proton reduction catalyst.

Fig. 4 shows a general scheme that utilizes a wide-band capturing, charge stabilizing donor-acceptor system coupled with a water oxidation catalyst (WOC) at the donor site and proton reduction catalyst (PRC) at the acceptor site for photocatalytic water-to-hydrogen production. In the grand scheme of solar-fuel production, the donor-acceptor system primarily serves as a photocatalyst. Few attempts have been made in the literature to establish such a solar-fuel producing nano-machines [64-66], however, much work needs to be done before a functional prototype machine capable of producing fuel in an economically competitive fashion could be realized. Key issues include development of modular and configurable routes to link the various components together for attain high performance, reliable and robust WOC, thus, demanding more work in this area of research.

1.5 Chromophores used in artificial photosynthetic systems

Porphyrins have widely been utilized in the field of artificial photosynthesis because of their unique properties and response to photo-irradiation. Porphyrins are rigid, square planar molecules made of four pyrroles connected to each other via methine bridges to form a larger ring structure (Fig. 5a). These molecules are stabilized by highly conjugated aromatic characteristics which extend through the entire structure. Porphyrins can form very stable

metal complexes with various metals using the four nitrogen atoms from the pyrrole entities. The

Fig. 5. Common photosensitizer donor and acceptor molecules used in building supramolecular energy harvesting ensembles.

chemical as well as physical properties of porphyrin can be tuned by the use of various metals for the central atom and peripheral substitution. Porphyrins are characterized by an absorption band in the 420 – 450 nm range (Soret region) with a very high molar absorption coefficient and less intense Q bands in the longer wavelength region of 500 – 700 nm [67-68].

Phthalocyanines are analogues of porphyrins possessing highly conjugated 18 π -electron planar aromatic systems, with a central cavity of sufficient size to accommodate various metal ions, and have also been widely used in building artificial photosynthetic systems (Fig. 5b). In phthalocyanine, the four indole units are in conjugation through the bridging nitrogen atoms to form a macrocyclic ring structure [69-70]. In phthalocyanines, the Q-band around 600 – 750 nm range is highly intense compared with the Soret band located in the 300 – 400 nm range. Phthalocyanines, having absorption beyond 1000 nm have also been synthesized and studied by changing the central metal atom as well as the peripheral substituents [71]. Phthalocyanines are thermally and chemically stable compounds having near-IR absorption and quantum yields higher than porphyrins. These features make phthalocyanines excellent candidates in building

the donor-acceptor ensembles. They can be employed as an antenna systems to absorb light in the near-IR region of the solar spectrum with a very high molar extinction coefficient ($200,000 \text{ M}^{-1} \text{ cm}^{-1}$). Advantageously upon photoexcitation, phthalocyanines act as very good electron donors [72].

1.6 Nanocarbons - elegant electron acceptor materials

Fullerenes, the first molecular allotropes of carbon was first made in 1985 and have profoundly influenced not only the area of chemistry but also the areas of biology, physics, and engineering. Fullerene, and in particular readily available C_{60} (Fig. 5c), exhibit a wide range of physical and chemical properties which makes them excellent building blocks for developing supramolecular assemblies. Functionalization of the spherical carbon surface leads to a plethora of unprecedented new molecular structures [73-74]. The unique physical and chemical properties of C_{60} , such as absorption in UV/Visible range, efficient singlet oxygen sensitizing ability, strong electron acceptor property, and superconductivity upon doping with alkali metals makes it a prominent candidate to be incorporated in different molecular designs [75-76]. Furthermore, its symmetrical shape, large size, and properties of its ?? - electronic structures influence substantially in the electron transfer processes (charge separation and recombination) [77]. It has already been confirmed that C_{60} and C_{70} are capable of accommodating six electrons potentially forming a diamagnetic C_{60}^{6-} species in CH_3CN /toluene solution, with the first reduction potential of C_{60} at -0.44 V vs SCE for the reversible formation of radical anion [78]. The fullerene C_{60} absorbs strongly in the UV region with molar extinction coefficient $100,000 \text{ M}^{-1} \text{ cm}^{-1}$ observed at 263 and 343 nm and a very weak absorption in visible region with molar extinction coefficient of $710 \text{ M}^{-1} \text{ cm}^{-1}$. Photoexcitation of C_{60} yields singlet excited $^1\text{C}_{60}^*$ that quantitatively converts to triplet excited $^3\text{C}_{60}^*$ [79-82]. Incorporating functional groups on C_{60} to enhance its solubility in common organic solvents has been achieved through a wide variety of addition reactions [21]. Among them, 1,3-dipolar cycloaddition of azomethine ylides, often known as Prato reaction, have been used extensively for versatile preparation of a large number of C_{60} derivatives, known as fulleropyrrolidines [83-86].

In addition to fullerenes, carbon nanotubes (Fig. 5d), endohedral fullerene, and graphene have also been employed as electron acceptors, and these have shown some promise towards building functional energy harvesting materials [87-90]. Known examples where metal-ligand axial coordination approach has been utilized to build donor-acceptor systems using these nanocarbon materials is also discussed as part of this review article.

For covalently linked systems and their potential applications, the readers are encouraged to consult references 91-100.

2 Non-covalently linked donor – acceptor systems

The covalent bonding approach of building supramolecular artificial photosynthetic systems differ from natural systems wherein the different photo and redox active components are held together non-covalent interactions. In such self-assembled ensembles, the donor and acceptor moieties remain close to each other through different non-covalent interactions and undergo light induced energy and electron transfer processes. The frequently found non-covalent interactions in such assemblies are hydrogen bonding, metal ligation, and π - π stacking which are considered as biomimetic methodologies. The major criteria for designing such non-covalent self-assemblies are the strength and directionality of the interaction which lead to efficient energy and electron transfer processes upon photoexcitation. As pointed out earlier, in this review, we focus our attention on the study of supramolecular donor-acceptor systems held together metal – ligand axial coordination.

2.1 Metal – ligand axial coordination as a general approach

A vast majority of the metals from the periodic table are capable of forming metal complexes with tetrapyrroles of square planar geometry, such as porphyrins and phthalocyanines. In several instances, the central metal atom in these complexes is coordinatively unsaturated thus exhibiting their desire for additional one or two ligands. Often, a second molecular entity (energy or electron acceptor/donor) is functionalized with a nitrogenous ligand and allowed to bind to such metal tetrapyrrole complexes. This metal-ligand axial interaction provides moderate to high stability for the resulting supramolecular light energy harvesting systems.

2.2 Models to probe excitation energy transfer

Porphyrins and phthalocyanines are ideal artificial light energy harvesting pigments because of their structural similarity to the natural photosynthetic pigments and advantageous photophysical and photochemical properties. Metal derivatives of porphyrins and phthalocyanines have widely been used to construct supramolecular self-assembled systems. By taking advantage of the metal-ligand axial coordination, in which the nitrogen coordinates to the central metal atom to form a supramolecular systems have been designed and studied.

Maligaspe et. al. [101] have designed and studied donor-acceptor dyads using free-base porphyrins as energy donors with zinc phthalocyanine and zinc naphthalocyanine as energy acceptors via metal-ligand axial coordination. To achieve the axial coordination, the free-base porphyrin was functionalized with an imidazole entity at the ortho, meta, or para position of one of the *meso*-aryl groups to visualize the effect of orientation in energy transfer, as shown in Fig. 6.

Upon increasing addition of H₂P(o, m, p)Im to a solution of ZnPc or ZnNc, changes in absorption spectra with isosbestic points were observed in *o*-dichlorobenzene (DCB) which indicated binding of porphyrins to ZnPc and ZnNc via metal-ligand axial coordination. From the changes, the stability constant was calculated and found to follow the order: para ≈ meta > ortho for the position of imidazole on porphyrin due to the imposed steric constraints. The orientation between donor and acceptor also played a key role on excitation transfer. Diminishing the fluorescence intensity of porphyrins upon increasing addition of either ZnPc or ZnNc have further supported the formation of donor-acceptor complexes via metal-ligand axial coordination as well as singlet excitation energy transfer from donor to acceptor. The Förster energy transfer mechanism was proposed wherein the rate constant for energy transfer was calculated using the following equation:

$$k_{\text{Förster}} = \frac{8.8 \times 10^{-25} \cdot \kappa^2 \cdot \phi_D \cdot J_{\text{Förster}}}{n^4 \cdot \tau_D \cdot R_{\text{DA}}^6} \quad (1)$$

where n = solvent refractive index, τ_D = fluorescence lifetime for donor, $J_{\text{Förster}}$ = spectral integral overlap, R_{DA} = center-to-center distance between the donor-acceptor entities.

Fig. 6. Structure of donors (porphyrins with imidazole group at different positions ortho-H₂P_oIm, meta-H₂P_mIm, and para-H₂P_pIm), and acceptors zinc phthalocyanine (ZnPc) and zinc naphthalocyanine (ZnNc) (adapted from Ref. 101).

From the computational study, the relative orientation of donor and acceptor was arrived and a **near** coplanar geometry for H₂P_oIm with ZnPc and ZnNc was observed while the complex with meta and para functionalized H₂PIm was positioned at an angle less than 90⁰. The kinetics of energy transfer were calculated using transient absorption spectroscopy through both up-conversion and pump-probe methods. The study revealed ultrafast energy transfer in the donor-acceptor dyads with time constants on the order of 2 – 25 ps depending upon the type of dyad, as shown in **Table 1** below. Similar results were obtained when ZnPc and ZnNc were replaced by MgPc and MgNc in DCB [102].

In the above example, the complexes designed by free-base porphyrin and zinc phthalocyanine via metal-ligand axial coordination were not stable enough to isolate due to the labile nature of the connectivity. Hence, only the dyads were possible to construct while polyads having multiple energy donors as a biomimetic multicomponent energy funneling antenna systems **were not synthetically accessible**. To overcome this issue Jacobs et.al. [103]

have designed dyads and a pentad bearing ruthenium carbonyl phthalocyanines, Ru(CO)Pc, which can be isolated and studied instead of zinc or magnesium analogs, as shown in Fig. 7.

The porphyrin and phthalocyanine dyads were comprised of 2-, 3-, or 4-imidazolyphenyl-substituted free-base porphyrin coordinated with Ru(CO)Pc, whereas the pentad was comprised of a porphyrin functionalized with four entities of 4-imidazolyphenyl substituted porphyrin coordinated with four Ru(CO)Pc. The choice of CO group on Ru(CO)Pc provided an extra ligation effect due to the π -acceptor nature of the carbonyl ligand at one end of the two axial Ru(II)

Table. 1. Estimated ($k_{\text{Förster}}$) and experimentally determined (k_{ENT}) rate constants of energy transfer for the dyads formed by coordination of imidazole appended free-base porphyrin to zinc phthalocyanine or zinc naphthalocyanine in DCB [101].

Dyad	$k_{\text{Förster}}, \text{s}^{-1}$	$k_{\text{ENT}}, \text{s}^{-1}$
H ₂ P _o Im:ZnPc	3.94 x10 ¹¹	1.4 x10 ¹¹
H ₂ P _m Im:ZnPc	1.32 x10 ¹¹	1.7 x10 ¹⁰
H ₂ P _p Im:ZnPc	2.30 x10 ¹¹	3.3 x10 ¹⁰
H ₂ P _o Im:ZnNc	3.88 x10 ¹¹	2.0 x10 ¹¹
H ₂ P _m Im:ZnNc	1.41 x10 ¹¹	9.0 x10 ¹⁰
H ₂ P _p Im:ZnNc	1.50 x10 ¹¹	4.0 x10 ¹⁰

coordination sites. The optical absorption spectrum in toluene revealed the characteristic free-base porphyrin and metallated phthalocyanine absorption bands of both H₂PIm and Ru(CO)Pc. H₂P_xIm (x = o, m, p) with a Soret band at 418 nm along with four less intense visible bands. Ru(CO)Pc had a strong Q band at 650 nm accompanied by weaker absorption bands at 587 and 346 nm. For the dyads, a 1:1 ratio of Soret band of porphyrin and the Q band of Ru(CO)Pc was observed. For the pentad, a ratio of porphyrin to Ru(CO)Pc was approximately 1:4 indicating the formation of pentad. The fluorescence spectra of the dyads and pentad were recorded in toluene by exciting at the Soret band of porphyrin which revealed a 95 to 97% fluorescence quenching of

Fig. 7. Structure of $H_2PIm:Ru(CO)Pc$ dyads and pentad. (adapted from Ref. 103).

porphyrin from their initial intensity. This was accompanied by red-shifts of 6 nm for the dyads and 12 nm for the pentad. The red-shift for the emission arising from porphyrin in the dyads and pentad was supportive of the formation of a complex via metal-ligand axial coordination [103]. The redox potentials of both dyads and the pentad were recorded in DCB containing 0.1 M TBA(ClO)₄. The dyad $H_2P_pIm:Ru(CO)Pc$, revealed four oxidation peaks at 0.62, 0.80, 1.09 and 1.45 V vs. Ag/AgCl and four reduction peaks located at - 1.12, - 1.20, - 1.49, and - 1.58 V vs. Ag/AgCl. By comparing the redox values of pristine $Ru(CO)Pc$ and H_2P , the first and fourth oxidations and second and fourth reductions correspond to $Ru(CO)Pc$ while second and third oxidations and first and third reductions correspond to H_2P . Very similar redox properties were displayed by the other two dyads. Due to the presence of four $Ru(CO)Pc$ entities in the pentad,

the current to which the redox peaks of H₂P assigned appeared as a shoulder peaks. The structure of all three dyads were optimized by using the B3LYP/3.21G(*) computational method which

Fig. 8. B3LYP/3-21(G*) optimized structure of a) H₂P_pIm:Ru(CO)Pc and b) H₂P_pIm:Ru(CO)Pc₄ pentad. The HOMO and LUMO of respective compounds are shown on the left and right side of each optimized structure. (reproduced with permission from Ref. 103).

revealed the porphyrin and phthalocyanine rings were in almost coplanar to orthogonal arrangement. The center-to-center distance between both of the macrocycles was in the order of ortho < meta < para imidazole substituted porphyrins. In the case of the pentad, H₂P_pIm:(Ru(CO)Pc)₄, the peripheral imidazole coordinated Ru(CO)Pc entities were positioned about 50° relative to the plane of the porphyrin ring. The frontier orbitals of both dyads and pentad were calculated and revealed the HOMO for all the polyads is fully localized over Ru(CO)Pc while the LUMO is localized over the porphyrin macrocycle, as shown in Fig. 8.

Subsequently, using pump-probe transient spectroscopic technique, confirmation on the mechanism and kinetics of the energy transfer process was secured for all the dyads and

pentad. Upon excitation with 420 nm wavelength light, $\text{H}_2\text{P}_m\text{Im}:\text{Ru}(\text{CO})\text{Pc}$ immediately generated three characteristic negative bands at 515, 550 and 585 nm due to the Q band bleaching of porphyrin. After two ns, two Q band bleaching peaks at 585 and 645 nm were observed corresponding to the phthalocyanine entity concurrent with the recovery of the previously mentioned negative bands indicating the occurrence of energy transfer process from porphyrin to phthalocyanine. During the course of the energy transfer process, the band at 720 – 730 nm was observed right after the singlet porphyrin peak decay, corresponding to the characteristic triplet state of $\text{Ru}(\text{CO})\text{Pc}$ [103]. As stated earlier, the energy transfer process occurs between porphyrin and phthalocyanine via singlet-singlet energy transfer. But because of the fast intersystem crossing of $\text{Ru}(\text{CO})\text{Pc}$, generally within 3 – 5 ps, i.e. faster than the energy transfer, the singlet excited state of $\text{Ru}(\text{CO})\text{Pc}$ was not observed as it was converted almost instantly to the triplet state. Interestingly, in the polar benzonitrile, a broad band located at 690 – 780 nm was observed corresponding to $\text{Ru}(\text{CO})\text{Pc}$ radical cation, while at the same time a band at 570 nm was observed corresponding to the porphyrin radical anion. This indicated the occurrence of electron transfer process within the dyad in the polar solvent. The other two dyads, $\text{H}_2\text{P}_o\text{Im}:\text{Ru}(\text{CO})\text{Pc}$ and $\text{H}_2\text{P}_p\text{Im}:\text{Ru}(\text{CO})\text{Pc}$, revealed similar spectral features to the $\text{H}_2\text{P}_m\text{Im}:\text{Ru}(\text{CO})\text{Pc}$ in both toluene and benzonitrile solvent. The kinetics of the energy transfer process in the pentad were also studied in toluene which revealed the occurrence of energy transfer process from porphyrin to phthalocyanine with a time constant of 26 ps which was followed by fast intersystem crossing to generate triplet $^3\text{Ru}(\text{CO})\text{Pc}^*$. Unlike the dyad, no evidence for electron transfer was observed in polar benzonitrile where only an energy transfer process was evident.

Fig. 9. Structure of porphyrin and phthalocyanine based dyad and pentad. M = H₂ and Zn. (adapted from Ref. 104).

To establish the self-assembled donor-acceptor systems to study photoinduced energy or electron transfer processes in supramolecular conjugates, a dyad and pentad consisting of pyridyl porphyrin and Ru-phthalocyanines self-assembled via metal-ligand axial coordination between pyridyl group and the Ru metal atom at the ratio of 1:1 and 1:4, respectively, was designed and their light energy harvesting properties were studied [104]. As shown in **Fig. 9**, the dyad consisted of a self-assembled mono pyridine appended porphyrin which was coordinated to the central Ru atom of a phthalocyanine molecule. The two pentads consist of a free-base or zinc porphyrin appended with 4-pyridyl groups at the periphery which axially coordinated to Ru atoms of four phthalocyanine entities.

The *meso* positions of mono and tetra-pyridyl appended porphyrins were covalently connected with 19 and 16 electron withdrawing fluorine atoms on the phenyl ring spacers, respectively. The absorption and fluorescence spectra of all three individual molecules along with the dyads and pentads were recorded in toluene and suggested occurrence of photoinduced energy transfer process from the porphyrin to phthalocyanine in all conjugates.

Further, femtosecond transient absorption spectra was recorded for all the complexes and their individual counterparts. Excitation of the $\text{ZnP}-(\text{Py})_4\text{:Ru(CO)Pc}_4$ pentad at 420 nm revealed a negative band at 560 nm along with positive bands located at 465, 605, and 695 nm. With time new minima transient bands developed and were located at 590 and 650 nm corresponding to Ru(CO)Pc ; this is due to the energy transfer from the porphyrin moiety to the phthalocyanines. Similarly, excitation of the $\text{H}_2\text{Por-Py}_4\text{:Ru(CO)Pc}_4$ at 420 nm revealed ground state bleaching at 510 nm and transient maxima at 460, 615, and 690 nm. After a time delay, the negative bands at 590 and 650 nm from Ru(CO)Pc recovered revealing the occurrence of intramolecular energy transfer process from the porphyrin to RuPc moiety.

2.3 Models to probe sequential energy/electron or electron/electron transfer

Various light energy harvesting systems mimicking light induced energy and electron transfer processes have been designed via metal-ligand axial coordination and studied through their photophysical and photochemical properties. The most common singlet excited state electron transfer process between donor and acceptor within the system is monitored and confirmed by absorption and fluorescence spectroscopy. Well-defined computerized modeling technique has often been used to identify the most stable geometry of the systems. The thermodynamic feasibility of a photoinduced electron transfer process is confirmed by electrochemical and spectral studies, and free-energy calculations. Finally, the kinetics of charge separation and the lifetime of the charge-separated states were evaluated by studies involving transient absorption spectroscopy.

Monodentate fullerene based axial ligated donor-acceptor systems. To study the photoinduced energy and electron transfer processes, a polyad comprised of four covalently linked carbazole units on the periphery of the central zinc phthalocyanine was synthesized and studied (see Fig.10A for structure) [105]. Upon photoexcitation of the carbazole unit, initial photoinduced energy transfer from the singlet excited state of carbazole to the central phthalocyanine was confirmed by steady-state spectroscopic techniques. The spectral overlapping of the emission and absorption spectra collected from the carbazole and ZnPc moieties, respectively, also supported energy transfer. In order to investigate photoinduced electron transfer process via metal-ligand axial coordination within the system, C_{60} , as an

electron acceptor chemically functionalized with a phenyl imidazole group, C₆₀Im was used. The imidazole group of the C₆₀ moiety axially coordinated with the central zinc of ZnPc to form an equilibrium complex with a stability constant of $7.7 \times 10^5 \text{ M}^{-1}$ which was calculated via the Benesi-Hildebrand method, using the absorption titration spectral data. Similarly, the observation of fluorescence quenching of ZnPc upon the addition of imidazole functionalized C₆₀, indicated the formation of a complex via metal-ligand axial coordination.

Fig. 10 (A) Structure of tetracarbazole appended ZnPc axially coordinated with C₆₀Im. (B) (a) Nanosecond transient absorption spectra observed by 505 nm laser irradiation of tetracarbazole appended ZnPc in the presence of C₆₀Im in N₂-saturated DCB. (b and c) Absorption time profiles of the 860 and 1000 nm bands; red lines are the first-order fitting curves. (adapted from Ref. 105).

In order to further confirm the electron transfer process, nanosecond transient absorption spectroscopic technique was used. Upon photoexcitation of the conjugate, two predominant peaks at 860 and 1010 nm were observed in the transient absorption spectrum due to the occurrence of photoinduced electron transfer process (see Fig. 10.B for spectra). The peak at 860 nm corresponded to an one-electron oxidized ZnPc (ZnPc^{•+} radical cation). The peak

at 1000 nm corresponds to an one-electron reduced C_{60} ($C_{60}^{\cdot-}$ radical anion). The kinetics of charge separation and recombination between ZnPc and C_{60} Im were calculated by monitoring time profiles of both the cationic and anionic radical peaks. Relatively fast charge separation and a slow charge recombination with rate constants of $2.8 \times 10^9 \text{ s}^{-1}$ and $6.25 \times 10^7 \text{ s}^{-1}$, respectively, was observed, which makes this system an ideal light energy harvesting conjugate.

The advantage of using multi-chromophoric systems is in their ability to harvest a wide range of the solar spectrum for optical and photovoltaic applications. Many research group have tried various non-covalent supramolecular assemblies bearing donor and acceptor systems to harvest light energy. Periera et. al. [106] have designed various porphyrin-phthalocyanine dyads covalently connected through pyrrolic positions of porphyrins as a donor that also self-assembled via metal-ligand axial coordination with C_{60} functionalized with pyridine group as an acceptor (Fig. 11).

Three derivatives of Por-Pc dyads were designed consisting of H_2P -ZnPc, ZnP-ZnPc, and PdP-ZnPc as an electron donors. Concurrently, two derivatives of C_{60} functionalized pyridyl groups, i.e. C_{60} -N-Py and C_{60} Py, were designed as electron acceptors. The absorption spectrum of all three P-Pc dyads were recorded in toluene which revealed the presence of an intense porphyrin Soret band in the range of 400-450 nm along with the Q bands located in the range of 500-600 nm. An intense band and a Soret band were also located at 680 nm and 350 nm, respectively. A red-shift of both bands (3 – 5 nm) compared with individual entities (pristine P and Pc) confirmed ground state electronic interactions between the two macrocycles in the dyad. Further, the fluorescence spectrum of the dyad revealed occurrence of singlet excitation transfer from porphyrin to phthalocyanine on selective excitation of the porphyrin. The energy transfer process in the dyads was studied by exciting the porphyrin band and was confirmed by observing significant quenching of porphyrin emission and concurrent appearance of phthalocyanine emission. Both absorption and emission titrations were performed in DCB on the self-assembled complexes of P-Pc dyads and fullerene derivatives. No appreciable changes on the spectrum were noted for the absorption titration of H_2P -ZnPc and PdP-ZnPc with both derivatives of C_{60} . However, the red-shift of 5 nm of the Soret band from ZnP-ZnPc along with the appearance of an isosbestic point at 420 nm was observed upon the addition of C_{60}

derivatives, which indicated formation of the complex. The formation constants of the complexes were 6.12×10^4 and $3.53 \times 10^3 \text{ M}^{-1}$ for $\text{C}_{60}\text{-N-Py}$ and C_{60}Py binding, respectively. Similarly, fluorescence quenching from the complex was observed when a fluorescence titration was performed.

Fig.11. Structure of porphyrin-phthalocyanine, P-Pc dyad and $\text{C}_{60}\text{-N-Py}$ and C_{60}Py . M = H₂, Zn and Pd. (adapted from Ref. 106).

Later, transient absorption spectroscopic studies were performed on both P-Pc dyads and various P-Pc:C₆₀ complexes to evaluate the kinetics of energy and electron transfer processes by exciting at 420 nm. Upon excitation of the ZnP-ZnPc dyad, a porphyrin singlet-singlet excited state peak was observed in the 440-500 nm region within 21 ps. In the red region, phthalocyanine peaks developed concomitantly, located in the 600-800 nm region with the decay of the porphyrin singlet-singlet peak, which suggested the occurrence of energy transfer process in the dyad from ZnP to ZnPc. Similar energy transfer processes were observed for other dyads. The transient absorption spectra of the complexes were recorded after the addition of C₆₀ derivatives to all dyads. Upon excitation of the dyad ZnP-ZnPc with 420 nm wavelength of light, after addition of $\text{C}_{60}\text{-N-Py}$ and C_{60}Py , positive transient bands located at 450 and 600 nm and negative bands located at 520 and 580 nm from porphyrin excited state were observed. These bands were short-lived and rapidly transformed into the phthalocyanine singlet excited state. The lifetime of the singlet excited state of porphyrin obtained from H₂P-ZnPc and PdP-ZnPc could not be evaluated because of the immediate formation of the triplet excited state. As the singlet excited state of porphyrin decayed, the singlet excited state of

phthalocyanine was generated, which underwent an intramolecular charge transfer process to give the $\text{ZnPc}^{\cdot+}$ cation and $\text{C}_{60}^{\cdot-}$ anion radical pair peaks located at 840 and 1010 nm in transient spectra, respectively. The final charge separation of the complex was observed in the form of $\text{ZnP-ZnPc}^{\cdot+}:\text{C}_{60}^{\cdot-}$ (Py or N-Py). Similar results were obtained for all complexes formed by donor dyads complexed with electron acceptor pyridine-appended fullerene derivatives.

Fig. 12. (a) Structure of TPA-BDP-ZnP axially coordinated with C_{60}Im . (b) Structure of TPA-BDP-ZnP axially coordinated with pyridyl naphthyl diimide (NDIPy) to study photoinduced energy and electron transfer processes. (adapted from Ref. 107).

To explore more towards the design and synthesis of multimodular donor-acceptor conjugates via metal-ligand axial coordination, a triad comprised of covalently linked triphenylamine (TPA), BODIPY (BDP), and porphyrin units was designed and studied whose structures are shown in **Fig. 12** [107]. A sequential and efficient multistep energy transfer from TPA to BDP to porphyrin was observed upon photoexcitation of TPA due to the perfect overlap of excitation and emission spectra of all components within the system. The absorption study of the triad in DCB clearly revealed a band at 310 nm corresponding to TPA, three bands at 427,

554 and 595 nm corresponding to porphyrin's Soret and Q bands, and a band at 510 nm corresponding to the BDP entity. Upon selective excitation of BDP, the emission intensity of BDP in the triad was diminished by 4.5 times when compared to that of pristine BDP. At the same time, the appearance of ZnP emission suggested the occurrence of excited state energy transfer from $^1\text{BDP}^*$ to ZnP. Because of the close proximity and favorable orientation between the BDP and ZnP moieties, ultrafast excited state energy transfer occurred with the rate constant of $k_{\text{ENT}} = 1 \times 10^{12} \text{ s}^{-1}$.

To investigate the electron transfer process in the conjugates, C_{60} functionalized with phenyl imidazole (C_{60}Im) and naphthalenediimide functionalized with pyridine (NDIPy), as shown in Fig. 12a and b, respectively, as electron acceptor were used to form complexes with the electron donor triad via metal-ligand axial coordination (Fig. 12). The electron donating N atoms from both electron acceptors coordinated with the central Zn atom of porphyrin in the triad. The formation of the donor-acceptor complex in DCB was established by steady-state absorption and fluorescence titrations. Absorption titration of C_{60}Im and NDIPy with the triad in solution revealed the characteristic spectral changes due to axial ligation where the absorption bands from ZnP were perturbed without disturbing the absorption band of BDP, thus indicating selective metal-ligand axial coordination. During the fluorescence titration, after axial coordination of C_{60}Im and NDIPy, the emission from ZnP was quenched suggesting the occurrence of an electron transfer process within the system. The binding constants, calculated by constructing Benesi-Hildebrand plots, were $K = 3.6 \times 10^3 \text{ M}^{-1}$ and $4.5 \times 10^3 \text{ M}^{-1}$ for C_{60}Im and NDIPy binding, respectively, with 1:1 molecular stoichiometry [107].

Both the femto- and nanosecond transient absorption techniques were performed in order to calculate the kinetics of the electron transfer process in the donor-acceptor conjugates. Upon binding of C_{60}Im to the triad, a transient band at 600 nm and 1000 nm corresponding to one-electron oxidized and reduced forms of ZnP and C_{60}Im , respectively, were observed. Similarly, upon binding of NDIPy with the triad, transient peaks at 490 and 600 nm corresponding to one-electron reduced and oxidized form of NDIPy and ZnP, respectively, were observed in toluene. Transient cation and anion features from BDP and TPA were not observed. This suggests that these components are not involved in the electron transfer process. The rate

constants for charge separation and recombination were calculated by analyzing the spectral data from transient experiments in both cases. The values of k_{CS} and k_{CR} for TPA-BDP-ZnP:C₆₀Im and TPA-BDP-ZnP:NDIPy in toluene were $5 \times 10^9 \text{ s}^{-1}$ and $2.1 \times 10^8 \text{ s}^{-1}$, and $3.47 \times 10^{10} \text{ s}^{-1}$ and $8.4 \times 10^8 \text{ s}^{-1}$, respectively. This revealed fast charge separation and relatively slow charge recombination processes in these systems.

To obtain a long-lived charge-separated state, a multicomponent self-assembled donor-acceptor system was designed consisting of fullerene functionalized with an imidazole group as an electron acceptor, axially coordinated to the zinc center of the ZnP-TPA-SubPc triad, which acted as both an energy transferring and charge stabilizing moiety. The SubPc and TPA molecules displayed higher energy singlet excited states which transfer energy to the ZnP moiety followed by an electron transfer from singlet excited ZnP to the axially coordinated C₆₀ to generate charge-separated states. The molecular structures of these self-assembled donor-acceptor systems are shown in Fig. 13 [108].

Fig.13. Structures of SubPc-TPA-ZnP triad and SubPc-TPA-ZnP:C₆₀Im self-assembled tetrad. (adapted from Ref. 108).

The absorption spectrum of the SubPc-TPA-ZnP triad was recorded in toluene which revealed characteristic absorption bands due to individual entities. The triad revealed bands located at 303 nm corresponding to TPA, 423 nm corresponding to ZnP Soret band, and 518 and 565 nm bands corresponding to SubPc Q bands. In the emission spectra, when SubPc band was selectively excited, the ¹SubPc* emission was significantly quenched while the emission from the ZnP entity was clearly detected due to the energy transfer process from ¹SubPc* to ZnP. The formation of a donor-acceptor complex was established by performing absorption and fluorescence titration experiments by the addition of imidazole functionalized C₆₀ to a solution of SubPc-TPA-ZnP. In the absorption spectral titration, upon addition of C₆₀Im, the Soret band revealed a 4 nm red-shift along with the appearance of an isosbestic point at 430 nm indicating formation of a complex via metal-ligand axial coordination. By monitoring the change in the absorption spectrum, the formation constant of the complex was evaluated as $K = 1.1 \times 10^4 \text{ M}^{-1}$. Similarly, the fluorescence titration of the triad with C₆₀Im was also performed, exciting the Soret band of ZnP, which revealed fluorescence quenching of the complex likely due to electron transfer process from the excited triad to the C₆₀Im moiety. To gain insight into the geometry and

Fig. 14. Frontier HOMO and LUMO orbitals of SubPc-TPA-ZnP:C₆₀Im self-assembled tetrad. (reproduced with permission from Ref. 108).

Electronic structure, the complex was optimized using B3LYP/6-31G* method. When the donor-acceptor complex was formed, the HOMO and HOMO-1 were located over the ZnP and TPA moieties, respectively, while the LUMO and LUMO+3 were located over the C₆₀Im and SubPc moieties, respectively, as shown in **Fig. 14**. This study suggests that ZnP and TPA molecules act as electron donors while the C₆₀Im acts as an electron acceptor to produce the SubPc-TPA-ZnP^{•+} - C₆₀Im^{•-} radical ion-pair **resulting from the** electron transfer process.

To further confirm the charge separation process in the complex, femtosecond transient absorption spectroscopic study was performed in benzonitrile and toluene solvents on both the triad and tetrad, as shown in **Fig. 15**. Upon excitation of the ZnP from the SubPc-TPA-ZnP triad using a 430 nm laser, transient absorption peaks in **the** visible region ascribed to the formation of initial charge-separated state were revealed as a SubPc^{•-}-TPA-ZnP^{•+} radical ion-pair. The femtosecond transient absorption spectra of the tetrad, after the addition of C₆₀Im, in toluene revealed clear transient bands located at 650 and 800 nm corresponding to the formation of TPA-ZnP^{•+} radical cation and a band at 1000 nm corresponding to the C₆₀Im^{•-} radical anion, generating the final charge-separated state, SubPc-TPA-ZnP^{•+}-C₆₀Im^{•-}. The time profile of the C₆₀Im^{•-} anion radical was monitored to calculate the rate constant of charge separation and recombination

Fig. 15. Femtosecond transient absorption spectra of SubPc-TPA-ZnP triad (top) and SubPc-TPA-ZnP:C₆₀Im tetrad (bottom) in toluene (reproduced with permission from Ref. 108).

processes, were 8.0×10^{11} and $6.3 \times 10^8 \text{ s}^{-1}$, respectively, with a 1.1 ns lifetime for the charge-separated state. Nanosecond transient absorption spectroscopy was performed on the tetrad to evaluate the lifetime of the charge-separated states at a longer time domain. Upon excitation of the ZnP moiety in toluene, the nanosecond transient spectra of the tetrad revealed the formation of $\text{ZnP}^{\cdot+}$ and $\text{C}_{60}\text{Im}^{\cdot-}$ radical ion pairs, respectively. The rate constant of charge recombination process was $1.6 \times 10^6 \text{ s}^{-1}$ and 6.6 μs , respectively. The achievement of such a long-lived charge-separated state was possible because the charge recombination process was in the Marcus inverted region.

A multicomponent supramolecular donor-acceptor triad composed of covalently linked $\text{ZnP}-(\text{BDP})_n$, ($n = 1, 2, 4$) axially bound to C_{60}Im was synthesized and studied as an artificial photosynthetic system to achieve long-lived charge-separated states by Maligaspe et.al. [109], (Fig. 16). Efficient excited state energy transfer from one, two, and four covalently linked BDP moieties to porphyrin followed by an electron transfer from excited ZnP to C_{60}Im was investigated. The synthesis of all the conjugates was achieved by connecting amine functionalized BDP at different ratios with the free-base porphyrin bearing different numbers of

meso-carboxyl acid groups (one, two, and four) through amide linkages, as shown in Fig. 16. The free-base porphyrin was subsequently metallated to form the zinc-porphyrin systems.

The electronic ground state interactions in all of the conjugates was established by recording the absorption spectra in DCB. In the dyad, triad, and tetrad, the observed bands at 426, 550, and 590 nm, correspond to ZnP while the band at 505 nm, corresponds to BDP absorption. As expected, the absorption intensity of the 505 nm peak was increased as the number of BDP units in the conjugates increased. The fluorescence emission spectrum of all the conjugates were recorded by exciting the BDP entity at 505 nm which showed a weak band in the range of 517 – 525 nm corresponding to BDP emission, and ZnP emission at 602 and 650 nm. The BDP emission was quenched by 96%, 93%, and 91% for BDP-ZnP, (BDP)₂-ZnP and (BDP)₄-ZnP, respectively, when compared with the pristine BDP moiety. The quenching of BDP emission and concomitant occurrence of ZnP emission indicated singlet-singlet energy transfer in all these conjugates.

Fig. 16. Structures of ZnP-(BDP)_n, (n = 1, 2, 4). (adapted from Ref. 109).

Optical absorption experiments and fluorescence titrations between (BDP)_n-ZnP with C₆₀Im were performed to establish the formation of supramolecular triad in solution via metal-ligand axial coordination in DCB. Upon the addition of C₆₀Im to a solution of (BDP)_n-ZnP, the Soret band of porphyrin in the absorption spectrum first decreased in intensity then increased with a red-shift to 431 nm along with the occurrence of two isosbestic points located at 422 and 429 nm indicating the formation of a supramolecular donor-acceptor complex in solution. Interestingly, the band at 495 nm corresponding to BDP was unperturbed during the course of the titration indicating absence of significant interactions of C₆₀Im with BDP. Next, fluorescence titration was performed by exciting the BDP moiety at 495 nm upon the addition of C₆₀Im, which revealed the quenching of emission bands from both BDP and ZnP. Fig. 17 shows the absorption and fluorescence titration of the (BDP)₂-ZnP triad vs C₆₀Im in DCB. Similar quenching was also monitored when the porphyrin band was excited which indicated the occurrence of a photoinduced electron transfer process from ZnP to C₆₀Im. This was later confirmed by a transient absorption experiment.

The dynamics of the excited state energy transfer in the (BDP)_n-ZnP conjugates was investigated by using the pump-probe spectroscopic technique. On photoexcitation of the BDP moiety of the BDP-ZnP dyad with a 500 nm excitation wavelength, a bleached band at 505 nm was observed with a time constant of 48 ps. At longer delay times, the 505 nm band decayed and new bands in the time resolved spectrum developed corresponding to the ZnP singlet excited state. The transient absorption spectra of the triad and pentad were similar to that of the dyad and the lifetime for excited state was determined to be 44 and 16 ps, respectively. These results obtained from the pump-probe technique suggest the occurrence of ultrafast singlet excitation energy transfer from covalently linked BDP to the ZnP moiety.

Fig. 17. (a) Absorption titration of $(\text{BDP})_2\text{-ZnP}$ triad with C_{60}Im . (b) Fluorescence titration of $(\text{BDP})_2\text{-ZnP}$ with C_{60}Im excited at 495 nm. The Fig. inset shows the Benesi-Hildebrand plot monitoring 520 nm to calculate the binding constant. (reproduced with permission from Ref. 109).

A relatively long-lived charge-separated state in artificial photosynthetic systems can be achieved by appending a hole shifting agent to the primary electron donor-acceptor pair. A tetrad composed of Fc-ZnP-BDP coordinated to C_{60}Im was designed and studied (see **Fig. 18** for structure) [110]. Here, the primary energy transfer process and electron transfer process occurred from $^1\text{BDP}^*$ to ZnP and from $^1\text{ZnP}^*$ to C_{60}Im , respectively. The hole shift was observed from Fc to oxidized ZnP to yield a long-lived charge-separated state as confirmed by transient absorption spectroscopy. The absorption spectrum of the Fc-ZnP-BDP triad was investigated in DCB which showed the typical ZnP absorption bands at 425 nm (Soret band), 550 and 590 nm (Q bands) along with a 505 nm band corresponding to BDP . The absorption band of Fc , located at 320 nm, was hidden under the strong absorption of ZnP and BDP in this region. The

fluorescence of the triad was investigated through selective excitation of 505 nm band of BDP which revealed a 95% fluorescence quenching of BDP with the appearance of two bands at 605 and 650 nm corresponding to ZnP emission suggesting the occurrence of energy transfer from $^1\text{BDP}^*$ to ZnP. The femtosecond transient spectrum of the triad revealed the appearance of a band in the range from 850 to 900 nm corresponding to $^1\text{ZnP}^*$, and a negative band at 510 nm corresponding to the ground state depletion of BDP. These bands further confirm the energy transfer process from $^1\text{BDP}^*$ to ZnP in the triad.

Fig. 18. A supramolecular tetrad featuring Fc-ZnP-BDP axially coordinated to C₆₀Im. Various photochemical events occurring in the chronological order upon photo-excitation are shown with the numbers. (adapted from Ref. 110).

The photoinduced electron transfer process in the tetrad, Fc-ZnP:ImC₆₀-BDP was investigated by complexing Fc-ZnP-BDP with C₆₀Im via metal-ligand axial coordination. The absorption titration of C₆₀Im with a solution of the triad was studied in DCB. Characteristic changes of metal-ligand axial coordination for peaks corresponding of ZnP were observed, however, the BDP band remained unchanged, thus, excluding the interaction of BDP with axially coordinated fullerene. The diminished fluorescence intensity from the triad after addition of C₆₀Im, upon selective excitation of the ZnP, suggested the occurrence of excited state photochemical events.

Fig. 19. (a) Femtosecond (b) nanosecond transient absorption spectroscopy of Fc-ZnP:ImC₆₀-BDP tetrad in toluene. (reproduced with permission from Ref. 110).

To investigate the electron transfer process within the supramolecular tetrad, Fc-ZnP:ImC₆₀-BDP femtosecond transient absorption technique was performed. Upon excitation at 400 nm, bands at 660 and 1000 nm were formed corresponding to the one-electron oxidized and reduced forms of ZnP and C₆₀Im, respectively (see Fig. 19a). The rate constant of charge separation was $k_{CS} = 5.9 \times 10^{10} \text{ s}^{-1}$. Interestingly, the decay of the ZnP^{•+} radical cation was faster compared to that of C₆₀^{•-} revealing occurrence of a hole shift process from closely spaced Fc to ZnP^{•+} to form Fc⁺ and ZnP. The energy level diagram also supported formation of Fc⁺ and C₆₀Im^{•-} radical ion-pairs as the final charge-separated state. Further, using nanosecond transient absorption technique (see Fig. 19b), the lifetime of the charge-separated state was obtained by monitoring the decay of C₆₀Im^{•-}. In toluene, the decay of C₆₀Im^{•-} was mono-exponential with a rate constant of $k_{CR} = 1.44 \times 10^5 \text{ s}^{-1}$. The decay of C₆₀Im^{•-} in DCB was bi-exponential due to the possibility of multiple geometries of the complex, giving two values for charge recombination $k_{CR} = 2.12 \times 10^5$ and $6.31 \times 10^4 \text{ s}^{-1}$. The lifetime of the charge-separated state of the complex varied from 7 – 15 μs depending upon the solvent.

Lim et.al. [111] further designed supramolecular donor-acceptor systems via metal-ligand axial coordination consisting of porphyrin-ferrocene dyads and triads (see Fig. 20). The porphyrin and ferrocene entities were separated by phenyl and amide linkages while the electron acceptor, C₆₀ was functionalized either with phenyl imidazole (C₆₀Im) or pyridine

(C₆₀Py). The role of Fc in these systems was to stabilize the charge-separated state by a hole shifting mechanism from the initial charge-separated state.

The formation of supramolecular complexes via axial coordination was monitored by absorption titration between ZnP-Fc dyads and C₆₀ derivatives in toluene. Upon addition of C₆₀ appended with Im or Py to a solution of ZnP-Fc, red-shifted Soret and visible bands accompanied by one or more isosbestic points were observed, suggesting the formation of donor-acceptor complexes via metal-ligand axial coordination. By monitoring the change in absorption, Job's and Scatchard plots were constructed. Job's plots revealed 1:1 complex formation while the Scatchard plots revealed the binding constant of the complexes in the range of 10³ M⁻¹.

Fig. 20. Structure of ZnP, ZnP-Fc dyads, C₆₀Py and C₆₀Im. (adapted from Ref. 111).

To establish the formation of photoinduced charge-separated states, femtosecond transient absorption studies were performed on all dyads and triads in toluene using a 400 nm laser with a 100 fs pulse width. Upon excitation of the ZnP-Fc dyad, a clear transient band located at 685 nm was observed corresponding to the ZnP⁻ radical anion with the estimated rate constant of charge separation (k_{CS}) and recombination (k_{CR}) as 7.90×10^{11} and 2.67×10^{10} s⁻¹.

¹, respectively. The transient spectrum of the triad Fc-ZnP-Fc also revealed a peak located at 680 nm corresponding to ZnP^{•-}. The values of k_{CS} and k_{CR} were found to be 8.64×10^{11} and $3.20 \times 10^{10} \text{ s}^{-1}$, respectively.

Fig. 21. Femtosecond transient absorption spectra of (a) ZnP-Fc:C₆₀Py and (e) ZnP-Fc:C₆₀Im in toluene at the excitation wavelength of 400 nm. Figures b, c and d show the time profile of 680, 726 and 1020 nm bands of ZnP-Fc:C₆₀Py, respectively, and f, g, and h show the time profile of 680, 722 and 1020 nm bands of ZnP-Fc:C₆₀Im, respectively. (reproduced with permission from Ref. 111).

To further investigate the kinetics and mechanism of the charge separation processes within the supramolecular dyads and triads after the addition of C₆₀Im or C₆₀Py, transient experiments were performed in toluene. The femtosecond transient absorption spectra of the tetrad, ZnP-Fc coordinated to C₆₀Py and C₆₀Im are shown in Fig. 21. New transient peaks located at 650 and 1020 nm corresponding to ZnP^{•+} and C₆₀^{•-} with a time constant of 24.4 ps for Fc-

ZnP:C₆₀Py and 33.68 ps for Fc-ZnP:C₆₀Im were observed. The rate constant for charge separation from ¹ZnP* to C₆₀ was 7.65 x 10¹¹ and 7.45 x 10¹¹ s⁻¹ for ZnP-Fc:C₆₀Py and ZnP-Fc:C₆₀Im, respectively. A similar experiment was performed on Fc-ZnP-Fc bound to C₆₀ (C₆₀Im or C₆₀Py). As expected, upon excitation of the conjugate, two clear transient peaks were observed at 1020 and 650 – 680 nm range corresponding to C₆₀^{•-} and ZnP^{•+}. The *k*_{CS} of the conjugates was evaluated to be 7.16 x 10¹⁰ and 6.54 x 10¹⁰ s⁻¹ for Fc-ZnP-Fc:C₆₀Py and Fc-ZnP-Fc:C₆₀Im, respectively. The rapid decay of ZnP^{•+} and the concurrent formation of C₆₀^{•-} radical anion suggested the electron transfer process to occur initially from Fc⁺-ZnP^{•+} to C₆₀ to generate Fc⁺-ZnP-C₆₀^{•-} as a final charge-separated state. The estimated rate constant for electron migration, *k*_{EM}, from ZnP^{•+} to C₆₀ was evaluated to be 7.38 x 10¹¹ and 6.16 x 10¹¹ s⁻¹ for Fc-ZnP-Fc:C₆₀Py and Fc-ZnP-Fc:C₆₀Im, respectively.

In another typical porphyrin-fullerene donor-acceptor system, aluminum porphyrin was used as a primary electron donor which was covalently connected with C₆₀-fullerene acting as an electron acceptor. This connection was via an ester linkage on one side of the porphyrin plane, while the other side of the plane was axially coordinated by tetrathiafulvalene, TTF functionalized with a pyridine group acting as a hole shift agent. Further, six vertical linear supramolecular triads, i.e. TTF-(Ph)_n(n=0,1):AlPor-(Ph)_n(n= 0,1,2)C₆₀, were designed, as shown in the Fig. 22. The distance-dependent sequential photoinduced electron transfer processes within the system were then systematically investigated [112]

Various spectroscopic techniques were used to establish the structural integrity of the complexes and kinetics of photoinduced electron transfer processes. The absorption spectrum of AlPor was recorded in DCB which revealed a Soret band at 415 nm and weak Q bands at 550 and 580 nm. The spectra of covalently linked dyads between AlPor and C₆₀ were also recorded which revealed spectral properties similar to pristine AlPor due to very weak ground state interactions between the two entities. The formation of complexes with TTF functionalized

$n = 0, m = 1$: TTF-py $\rightarrow$ AlPor-Ph-C₆₀
 $n = 1, m = 1$: TTF-Ph-py $\rightarrow$ AlPor-Ph-C₆₀
 $n = 0, m = 2$: TTF-py $\rightarrow$ AlPor-Ph₂-C₆₀
 $n = 1, m = 2$: TTF-Ph-py $\rightarrow$ AlPor-Ph₂-C₆₀
 $n = 0, m = 3$: TTF-py $\rightarrow$ AlPor-Ph₃-C₆₀
 $n = 1, m = 3$: TTF-Ph-py $\rightarrow$ AlPor-Ph₃-C₆₀

Fig. 22. Structure of various TTF-AlPor-C₆₀ supramolecular triads. (adapted from Ref. 112).

with pyridine was investigated by using optical absorption technique where TTFPy was added to a solution of AlPor-C₆₀. This revealed a significant change in both of the Soret and Q bands of AlPor as a result of metal-ligand axial coordination. By monitoring the change in absorption during the course of titration, a Benesi-Hildebrand plot was constructed to calculate the formation constant of the complexes which was in the range of 10^3 M^{-1} for all complexes. Similarly, the fluorescence titration between the same species was performed which revealed the quenching of AlPor [suggesting](#) the occurrence of photoinduced electron transfer from ¹AlPor* to C₆₀ followed by a hole shift from TTF to AlPor within the system. This was later confirmed by femtosecond transient absorption spectroscopy.

To investigate the various photoinduced events occurring in these donor-acceptor complexes, femtosecond transient absorption studies were performed in DCB using a

femtosecond laser system operating at 400 nm (Fig. 23). Upon excitation of the dyad, i.e. AlPor-C₆₀, two transient peaks at 450 and 1240 nm along with two negative peaks at 590 and 650 nm were observed. The decay of ¹AlPor* was accompanied by the formation of new bands at 1020 nm and 600 – 650 nm corresponding to the formation of C₆₀^{•-} and AlPor^{•+}, respectively. Further, the transient study of the supramolecular triad formed by coordination of TTFPy to AlPor-C₆₀ was also performed to characterize the final charge-separated state and determine its lifetime. Upon excitation of the triad, a new transient band emerged between 450 to 500 nm suggesting the formation of TTF^{•+} radical cation. As expected, the broad peak of AlPor^{•+} in the 600 nm range disappeared upon addition of TTFPy suggesting occurrence of hole shift process between AlPor^{•+} and TTF species. The decay of C₆₀^{•-} lasted beyond 3 ns – the limit for the fs transient absorption setup – suggesting the use of nanosecond transient absorption spectroscopic technique to

Fig.23. Femtosecond transient absorption spectra of (a) TTF-Py:AlPor-Ph₂-C₆₀ and (b) TTF-Ph-Py:AlPor-Ph₂-C₆₀ in toluene. Figs. c, d and e represent peak maxima time profiles of the 1240 nm band of ¹AlPor* for the investigated Alpor-Ph-C₆₀, AlPor-Ph₂-C₆₀ and AlPor-Ph₃-C₆₀ dyads in

the presence of TTF-Py and TTF-Ph-Py, respectively. (reproduced with permission from Ref. 112).

Table 2. Charge separation and recombination lifetimes from femtosecond and nanosecond transient absorption techniques (from Ref. 112).

Sample	<i>fs</i> -TA ^a		<i>ns</i> -TA ^c
	τ_{CS} (ps)	$k_{CS}^b (\times 10^9 \text{ s}^{-1})$	τ_{CR} (ns)
AlPor-Ph-C ₆₀	152	6.45	38
TTF-py→AlPor-Ph-C ₆₀	100	9.87	64
TTF-Ph-py→AlPor-Ph-C ₆₀	144	6.80	96
AlPor-Ph ₂ -C ₆₀	664	1.38	-
TTF-py→AlPor-Ph ₂ -C ₆₀	220	4.42	-
TTF-Ph-py→AlPor-Ph ₂ -C ₆₀	315	3.05	-
AlPor-Ph ₃ -C ₆₀	1620	0.49	-
TTF-py→AlPor-Ph ₃ -C ₆₀	196	4.97	-
TTF-Ph-py→AlPor-Ph ₃ -C ₆₀	330	2.91	-

^aIn Ar-saturated toluene. ^b $k_{CS} = 1/\tau_{\text{dyad}} - 1/\tau_{\text{ref}}$, where τ_{ref} is the lifetime of ¹AlPor* being 7.88 ns in toluene, here the τ values are decay constants of the 1240 nm peak corresponding to singlet-singlet transition of AlPor. ^cIn Ar-saturated dichlorobenzene.

characterize the final charge separation products. Upon excitation of the triad, TTF-Py:AlPor-Ph-C₆₀, in DCB saturated with argon using a 532 nm laser, a peak of C₆₀^{•−} at 1020 nm was observed. By monitoring the time profile of this peak, the rate constant for charge separation was calculated to be $1.57 \times 10^7 \text{ s}^{-1}$ (see Table 2). Another transient peak at 470 nm corresponds to TTF^{•+} radical cation. This peak was also monitored in order to calculate the rate constant of charge recombination as $1 \times 10^7 \text{ s}^{-1}$. This suggests that the initial charge separation in the system occurred between AlPor and C₆₀ to generate AlPor^{•+}-C₆₀^{•−} radical ion-pair followed by a hole shift from AlPor^{•+} to axially coordinated TTF generating the observed final charge separation state as TTFPy^{•+}:AlPor-C₆₀^{•−} radical ion-pair.

One of the issues while designing supramolecular donor-acceptor systems consisting of porphyrins and phthalocyanines is that they form aggregated species in solution, masking their inherent properties. Aggregation also results in reduced fluorescence quantum yield and lifetime of photosensitizers which restricts the use of such aggregated conjugates for the study of photoinduced energy and electron transfer processes. One elegant approach to overcome

this problem was to use metal-ligand axial coordination to minimize self-aggregation. In a study, Jana et. al. [113] designed an electron rich tetrathiafulvalene fused zinc porphyrin, (TTF)₄ZnP, as a donor that revealed appreciable self-aggregation (see Fig. 24 for structure). To break the intermolecular aggregation and form the donor-acceptor assembly, (TTF)₄ZnP was axially coordinated with C₆₀Im. Further this system was used to study the photoinduced electron transfer process.

Fig. 24. Structure of tetrathiafulvalene fused zinc porphyrin, (TTF)₄ZnP. (adapted from Ref. 113).

The absorption spectrum of (TTF)₄ZnP in DCB revealed a Soret band located at 448 nm with a shoulder band at 464 nm, and a broad Q band located in the range of 550 – 800 nm. The shoulder band was attributed to the self-aggregated species. The red-shifted Soret band of the newly synthesized (TTF)₄ZnP compared with ZnP (Soret band at 423 nm), was attributed to the extended π -system and charge transfer type of interactions between the fused TTF and ZnP moieties. The fluorescence spectrum of (TTF)₄ZnP recorded in the same solvent revealed two bands located at 610 and 668 nm with a significantly quenched intensity. The quenching of fluorescence intensity was attributed to both aggregation and intramolecular charge transfer between fused TTF and ZnP moieties. The formation of a complex between (TTF)₄ZnP and C₆₀Im was initially studied by performing absorption and fluorescence titrations in DCB. The absorption titration revealed broader Soret band while Q bands became narrower with a concurrent increase in intensity. The final complex, (TTF)₄ZnP:C₆₀Im, had Soret and visible bands

located at 460 and 583 nm, respectively. A Benesi-Hildebrand plot was constructed by monitoring the change in absorption and used to [determine](#) the binding constant which was $K = 2.1 \times 10^5 \text{ M}^{-1}$. Differential pulse voltammetry experiment was performed in DCB containing 0.1 M (TBA)ClO₄ as a supporting electrolyte. Upon complexation of (TTF)₄ZnP with C₆₀Im, no significant redox potential change corresponding to either C₆₀Im or TTF entities was observed. However, a 20 mV anodic shift of the oxidation peak of ZnP was observed after formation of the complex. Computational study performed by using B3LYP/3-21G* method on the complex (TTF)₄ZnP:C₆₀Im revealed HOMO and LUMO orbitals localized over TTF and C₆₀ moieties, respectively. The free energy change for photoinduced electron transfer process calculated by using redox, spectral and computational data revealed the formation of various charge-separated states, i.e. (TTF)₄ZnP^{•+}:C₆₀Im^{•-} and (TTF)₃-TTF^{•+}-ZnP:C₆₀Im^{•-} which were associated with a free energy change of -0.16 and -1.05 eV, respectively. Such calculations [suggested TTF acting as a hole](#) transfer agent to generate long-lived charge-separated state.

To observe the charge separation processes in the complex, both femto and nanosecond transient spectroscopic studies were performed in DCB. In the femtosecond transient absorption, shown in [Fig. 25](#), excitation of the complex, (TTF)₄ZnP:C₆₀Im, showed two clear transient bands located at 1000 nm and in the 650-700 nm range corresponding to C₆₀^{•-} and ZnP^{•+}, respectively. At higher delay times, another band at 570 nm corresponding to TTF^{•+} was observed with concurrent decay of ZnP^{•+}. These observations pointed out occurrence of a hole transfer process from ZnP^{•+} to one of the TTF molecules. By monitoring the time profile of C₆₀^{•-}, an ultrafast charge

Fig.25. (a) Femtosecond transient absorption spectra of (TTF)₄PZn:C₆₀Im in DCB. (b) Time profile of the C₆₀^{•-} radical anion peak monitored at 1000 nm. (reproduced with permission from Ref. 113).

separation process at a rate constant of $1.4 \times 10^{11} \text{ s}^{-1}$ was arrived. In order to calculate the exact rate constant of charge recombination, nanosecond transient absorption spectra of the complex was recorded in DCB. Upon excitation, peaks corresponding to (TTF)₃-TTF^{•+}-ZnP:C₆₀Im^{•-} charge-separated product was observed. Decay of the band at 1000 nm corresponding to C₆₀^{•-} was bi-exponential resulting in k_{CR} values of 3.3×10^7 and $2.5 \times 10^6 \text{ s}^{-1}$ with an associated lifetimes of 0.03 and 0.44 μs for the final charge-separated species.

Design of an ideal artificial photosynthetic system capable of collecting and harvesting light from the visible and near-IR regions of the electromagnetic spectrum is challenging. A significant effort has been made to design such types of molecular architectures. KC et.al. [114] designed and studied a multimodular broad-band capturing, charge stabilizing, photosynthetic model system comprised of a ZnP-ZnPc dyad held together an ether linkage as a primary electron donor. Additionally, three triphenylamine (TPA) entities were covalently connected at the *meso* positions on ZnP, as shown in **Fig. 26**.

The primary use of TPA groups in the model system was to capture the light energy from around 300 nm and funnel it to the porphyrin center in order to trigger further photochemical events and to stabilize the photoinduced charge-separated states. Finally, two C₆₀Im electron acceptors coordinated zinc metal centers of ZnP and ZnPc. The whole system is represented as (TPA)₃ZnP:ImC₆₀-ZnPc:ImC₆₀. The absorption study of the dyad (TPA)₃-ZnP-ZnPc was recorded in DCB which revealed prominent peaks located at 315, 348, 435, 556, 613, and 680 nm, where the first assigned peak corresponds to three TPA entities, the next two peaks correspond to ZnP, and last two peaks correspond to the ZnPc entity. The intensity ratio of 435 and 680 nm bands corresponding to the Soret and Q bands of ZnP and ZnPc, respectively, was at a 1:1 ratio.

To visualize the occurrence of sequential energy transfer processes, a fluorescence experiment was performed. Selective excitation of the TPA moiety at 315 nm revealed about 97% quenching while ZnP excitation revealed about 94% fluorescence quenching. In the final

spectrum, only an emission band at 694 nm corresponding that of ZnPc fluorescence was observed. This is indicative of a sequential energy transfer process taking place first from TPA to ZnP and second from ZnP to ZnPc. The sequential energy transfer process was further

Fig. 26. Structure of $(\text{TPA})_3\text{ZnP-ZnPc}$ along with mode of axial coordination of C_{60}Im to zinc centers. (adapted from Ref. 114).

confirmed by performing some other appropriate control experiments, viz., recording excitation spectra. To establish the formation of a donor-acceptor complex between $(\text{TPA})_3\text{ZnP-ZnPc}$ and C_{60}Im , both absorption and fluorescence studies were performed. The absorption titration performed in DCB by addition of C_{60}Im to a solution of $(\text{TPA})_3\text{ZnP-ZnPc}$ yielded the $(\text{TPA})_3\text{ZnP:ImC}_{60}\text{-ZnPc:ImC}_{60}$ complex. The initial decrease in the intensity of both the Soret band of ZnP and Q band of ZnPc along with the appearance of several isosbestic points revealed the complex formation process. The absorption titration data was utilized to evaluate the

binding constant of both metal centers by constructing Benesi-Hildebrand plots. By monitoring the change in absorption, the binding constants were evaluated to be 4.9×10^4 and $5.1 \times 10^4 \text{ M}^{-1}$, respectively for ZnP and ZnPc binding to C_{60}Im .

The fluorescence spectrum of $(\text{TPA})_3\text{ZnP-ZnPc}$ in the presence of C_{60}Im , excited at both ZnP and ZnPc, was recorded. This revealed the quenching of fluorescence of both ZnP and ZnPc entities suggesting the occurrence of a photoinduced electron transfer process in the system. An electrochemistry experiment was performed to calculate redox potentials of the conjugate in DCB containing 0.1 M $\text{TBA}(\text{ClO})_4$ as a supporting electrolyte. $(\text{TPA})_3\text{ZnP-ZnPc}$ revealed three oxidation peaks at -0.06, 0.11, and 0.80 V vs Fc/Fc^+ where first two correspond to ZnPc and last one to ZnP. Two reduction peaks located at -1.66, and -1.84 V vs Fc/Fc^+ were also revealed which correspond to ZnP and ZnPc reductions, respectively. This experiment was further continued upon the addition of C_{60}Im into the solution which formed $(\text{TPA})_3\text{ZnP}:\text{ImC}_{60}\text{-ZnPc}:\text{ImC}_{60}$ complex. Diminished current from the first oxidation processes of ZnP and ZnPc along with a 20 – 75 mV anodic shift, suggesting participation of both ZnP and ZnPc in conjugate formation was noted. Finally, transient absorption studies were performed to characterize the charge-separated products.

In the femtosecond transient absorption spectroscopy, the conjugate was first excited by 400 nm light in toluene which produced ground state depleted peaks at 440, 550, 610, and 678 nm in which first two peaks corresponded to ZnP and last two peaks corresponded to ZnPc ground state bleaching. Positive peaks located at 471, 576, 734, and 770 nm were also observed, as shown in Fig. 27a. With time, the intensity of the 440 and 550 nm peaks decreased with the concurrent increase in peak intensity of the 680 nm band corresponding to ZnPc fluorescence. This suggested the occurrence of energy transfer process from $^1\text{ZnP}^*$ to ZnPc with the rate constant of $k_{\text{ENT}} = 1.6 \times 10^{11} \text{ s}^{-1}$. Next, to probe the mechanism of photoinduced electron transfer processes in the conjugate, the femtosecond experiment was further performed on the $(\text{TPA})_3\text{ZnP}:\text{ImC}_{60}\text{-ZnPc}:\text{ImC}_{60}$ complex. In the first experiment, $(\text{TPA})_3\text{-ZnP-ZnPc}$ was complexed with only one equivalent of C_{60}Im . Upon excitation of the complex, three clear transient peaks were observed at 1020, 845, and 1360 nm corresponding to $\text{C}_{60}^{\cdot-}$ radical anion, $\text{ZnPc}^{\cdot+}$, and $\text{ZnP}^{\cdot+}$ radical cations, respectively, as shown in Fig. 27b. These results

suggest the formation of $(\text{TPA})_3\text{ZnP}^+:\text{ImC}_{60}^-$ -ZnPc:ImC₆₀ and $(\text{TPA})_3\text{ZnP}:\text{ImC}_{60}$ -ZnPc $^+:\text{ImC}_{60}^-$ radical ion-pairs although the process of formation of the complex is incomplete due to

insufficient supply of C₆₀Im. The decay profile of all three peaks was monitored and found that the 1360 nm peak, which corresponds to the $[(\text{TPA})_3\text{ZnP}]^+$ radical cation, decayed faster compared with the other peaks in the conjugate.

Fig. 27. Femtosecond transient spectrum of (a) $(\text{TPA})_3\text{ZnP}$ -ZnPc (inset: time profile of the 473 nm (blue) and 680 nm (red) peaks), (b) $(\text{TPA})_3\text{ZnP}$ -ZnPc in the presence of 1 eq. of C₆₀Im (inset: time profiles of 842 nm (blue) 1020 nm (magenta), and 1360 nm (wine) peaks), and (c) $(\text{TPA})_3\text{ZnP}$ -ZnPc in the presence of 2.2 eq. of C₆₀Im to form $(\text{TPA})_3\text{ZnP}:\text{ImC}_{60}$ -ZnPc:ImC₆₀ conjugate (inset: time profiles of 842 nm (blue) 1020 nm (magenta), and 1360 nm (wine) peaks). The time profile shown in Figure c inset at shorter delay times representing rise and partial decay of the radical signals while in Figure d are for shorter delay times. The red line shows the time profile at shorter delay times of $(\text{TPA})_4\text{ZnP}^+:\text{ImC}_{60}^-$ monitored at 1360 nm. The

spectra were recorded in toluene at the indicated time delays at an excitation wavelength of 400 nm. (reproduced with permission from Ref. 114).

Next, the transient spectra of (TPA)₃ZnP-ZnPc in the presence of 2.2 equivalents of C₆₀Im to form (TPA)₃ZnP:ImC₆₀-ZnPc:ImC₆₀ was recorded and characteristic peaks of radical ions were monitored, as shown in Fig. 27c. Within 10 ps, two peaks at 1360 and 1020 nm were developed corresponding to (TPA)₃ZnP^{•+} and C₆₀Im^{•-} species, respectively. A peak located at 840 nm later developed corresponding to ZnPc^{•+} radical cation. This result suggested the formation of (TPA)₃ZnP^{•+}:ImC₆₀^{•-} - ZnPc:ImC₆₀ radical ion-pair as the major initial product. The decay profile of (TPA)₃ZnP^{•+} was faster than the decay of ZnPc^{•+}, suggesting a hole shift process from (TPA)₃ZnP^{•+}:ImC₆₀^{•-}-ZnPc:C₆₀Im to ZnPc within the conjugate to yield (TPA)₃ZnP:ImC₆₀^{•-}-ZnPc^{•+}:ImC₆₀ radical ion-pair. Due to distant separation of radical cation and radical anion species in (TPA)₃ZnP:ImC₆₀^{•-}-ZnPc^{•+}:ImC₆₀, the final charge-separated state lifetime persisted beyond 3 ns. In order to further characterize the (TPA)₃ZnP:ImC₆₀^{•-}-ZnPc^{•+}:ImC₆₀ radical ion-pair, nanosecond transient absorption spectral studies were performed. The nanosecond spectrum of (TPA)₃ZnP:ImC₆₀-ZnPc:ImC₆₀ conjugate, recorded at a 32 and 68 ns delay time revealed two clear peaks at 840 and 1020 nm corresponding to ZnPc^{•+} and ImC₆₀^{•-} species, respectively. The lifetime of the final charge-separated state, i.e. (TPA)₃ZnP:ImC₆₀^{•-}-ZnPc^{•+}:ImC₆₀ formed after the CS/HS processes, was calculated to be 100 ns which was over 20 times greater than that reported for ZnPc^{•+}-ImC₆₀^{•-} radical ion-pair [114].

Bidentate fullerene based axial ligation: To mimic the energy and electron transfer events of natural photosynthetic processes, azaBODIPY (ADP) was covalently linked with two porphyrins via an ester linkage to generate a spatial arrangement featuring a molecular clip to host C₆₀ via metal-ligand axial coordination [115]. Here, C₆₀ was intentionally functionalized with two pyridine moieties to coordinate to both zinc porphyrins of the host system as shown in Fig. 28. Due to the large spectral overlap between zinc porphyrin emission and ADP absorption, energy transfer process was observed from ¹ZnP* to ADP in toluene. The absorption band intensity at 422 nm, corresponding to ZnP Soret band, and another band at 685 nm, corresponding to ADP's Q-band, were at almost a 2:1 ratio confirming the presence of

two ZnP moieties and one ADP molecule in the system. To investigate the energy transfer process within the system, the ZnP moiety was selectively excited. This produced an emission from the ZnP which was quenched dramatically along with the appearance of a new emission bands located at 735 nm corresponding to ADP emission. This suggests occurrence of energy transfer from $^1\text{ZnP}^*$ to ADP, which was further confirmed by recording the excitation spectrum. To get insight into the most favorable geometry of the triad, the molecule was fully optimized using B3LYP/3-21G(*) method revealing the flatness of both ADP and ZnP with a molecular clip type structure showing Zn – B – Zn angle of 60° which was suitable for hosting the bipyridine C_{60} guest.

Fig. 28. Structure of (a) ADP-(ZnP)₂ triad, and (b) ADP-(ZnP)₂:C₆₀Py₂ tetrad (adapted from Ref. 115).

To establish the formation of supramolecular tetrad, (ZnP)₂-ADP:C₆₀Py₂, absorption and fluorescence titrations were performed in DCB, a non-coordinating solvent. During the absorption titration, the ZnP Soret band showed diminished intensity with red-shifts, which was characteristic of axial coordination. Interestingly, the band at 667 nm corresponding to ADP remained unperturbed ruling out the role of ADP in metal-ligand axial coordination. Using the absorption titration data, the binding constant and molecular stoichiometry were evaluated. A binding constant of $K = 1.85 \times 10^5 \text{ M}^{-1}$ and 1:1 mole ratio for the supramolecular complex were obtained. This binding constant of bidentate C₆₀Py₂ binding to bis-porphyrin was about two orders of magnitude higher compared to the monodentate C₆₀Py binding to ZnP. This was due

to the two-point binding of the former case which holds the system more securely. The fluorescence studies revealed quenching of ZnP fluorescence upon addition of $C_{60}Py_2$, suggesting the occurrence of excited state events originating from $^1ZnP^*$.

Fig. 29. Femtosecond transient absorption spectra (excited at 420 nm) of $C_{60}Py_2:(ZnP)_2$ -azaBODIPY supramolecular tetrad in toluene. The inset shows the decay profile of C_{60} radical anion. (reproduced with permission from Ref. 115).

To investigate the fluorescence quenching mechanism, femtosecond transient absorption spectroscopic studies were performed in toluene. Upon selective excitation of the ZnP moiety of ZnP_2 -ADP: $C_{60}Py_2$ with a 420 nm excitation source, instantaneous formation of $^1ZnP^*$ was observed having a characteristic peak at 458 nm. Disappearance of this peak was accompanied by two distinctive peaks at 620 and 1000 nm corresponding to one-electron oxidized and reduced forms of ZnP ($ZnP^{\cdot+}$) and C_{60} ($C_{60}^{\cdot-}$), respectively (Fig. 29). These results confirmed the occurrence of photoinduced electron transfer process within the supramolecular system. The kinetics of electron transfer was evaluated by monitoring the time profiles of the peaks corresponding to $ZnP^{\cdot+}$ or $C_{60}^{\cdot-}$ radicals. A fast charge separation $k_{CS} = 6.2 \times 10^{10} \text{ s}^{-1}$ and relatively slow charge recombination rate of $k_{CR} = 1.8 \times 10^8 \text{ s}^{-1}$ was evident. The lifetime of the final charge-separated state ($C_{60}Py_2^{\cdot-}:ZnP_2^{\cdot+}$ -ADP) was about 5.5 ns. Finally, this system was subjected to build solar cells which revealed light-to-electricity conversion.

In another study, to investigate photoinduced energy transfer followed by an electron transfer processes, a dyad possessing ZnP and ZnPc covalently linked by an ester linkage was designed and synthesized [116]. The geometry of the dyad was held in a V-shape by connecting a ZnPc moiety to the meta position of one of the periphery phenyl rings of ZnP via an ester linkage. The two donor sites of the V-shaped dyad comfortably accommodated $C_{60}Py_2$, an electron acceptor. The pyridine rings of $C_{60}Py_2$ axially coordinated to the Zn metal centers of ZnP and ZnPc providing the thermodynamic stability and defined shape to the system via the two-point metal-ligand binding (Fig. 30).

Fig. 30. Supramolecular triad featuring V-shaped ZnP-m-ZnPc dyad axially coordinated to $C_{60}(Py)_2$. (adapted from Ref. 116).

The synthesis of the ZnP-ZnPc dyad was carried out by reacting a meta-carboxy ZnP with ZnPc-OH by a DCC coupling reaction. Due to complementary absorption and emission properties of ZnP and ZnPc entities in the dyad, energy transfer from $^1ZnP^*$ to ZnPc was observed. In the fluorescence study, the ZnP was selectively excited at 425 nm, the signature emission bands of ZnP moiety were quenched over 90% and a new band at 695 nm was observed corresponding to ZnPc fluorescence suggesting energy transfer from $^1ZnP^*$ to ZnPc. The energy transfer process was further confirmed by recording the excitation spectrum of the dyad. Next, the supramolecular triad was formed by complexing ZnP-m-ZnPc dyad with $C_{60}Py_2$, both absorption and emission titrations were performed as shown in Fig. 31. During the

addition of $C_{60}Py_2$ to ZnP-m-ZnPc in non-coordinating solvent DCB, the characteristic spectral changes of metal-ligand axial coordination were observed. That is, diminished absorption intensity accompanied by red-shifts of both ZnP and ZnPc bands with the appearance of isosbestic points were observed. Similarly, after the addition of $C_{60}Py_2$, the emission bands of the dyad were also quenched. The absorption and emission titration data were used to calculate the stoichiometry and binding constant of the system which revealed a 1:1 mole ratio for ZnP-m-ZnPc binding to $C_{60}Py_2$ and a binding constant of $1.7 \times 10^5 \text{ M}^{-1}$.

Fig. 31. (a) Absorption spectral changes observed for $C_{60}Py_2$ binding to ZnP-m-ZnPc in DCB, (b) Benesi-Hildebrand plot to calculate the binding constant, (c) Mole-ratio plot to establish the molecular stoichiometry, (d) Fluorescence changes observed for $C_{60}Py_2$ binding to ZnP-m-ZnPc in DCB; $\lambda_{ex} = 412 \text{ nm}$ corresponding to one of the isosbestic points. (reproduced with permission from Ref. 116).

To further investigate the occurrence of photoinduced electron transfer process within the system, femtosecond transient absorption spectroscopy was used. The dyad, upon

excitation with a 393 nm laser revealed the formation of $^1\text{ZnP}^*$ with characteristic transient peaks at 500 and 950 nm, which later decayed to populate $^1\text{ZnPc}^*$ with emission peak located at 830 nm, confirming the occurrence of the photoinduced energy transfer process. This process took place within 1.5 ps from $^1\text{ZnP}^*$ to ZnPc. To observe the electron transfer process within the system, the complex was excited again with a 393 nm laser after the addition of C_{60}Py_2 to the DCB solution of ZnP-m-ZnPc. Two characteristic transient bands appeared at 840 and 1000 nm corresponding to oxidized and reduced forms of ZnPc ($\text{ZnPc}^{\cdot+}$) and C_{60} ($\text{C}_{60}^{\cdot-}$) producing the final charge-separated states of $\text{ZnP-ZnPc}^{\cdot+} - \text{C}_{60}\text{py}_2^{\cdot-}$ that had a lifetime of about 3 ns.

In another example, a multimodular donor-acceptor system composed of two Zn-porphyrin and a ZnPc molecular triad was designed to study the energy transfer, and electron transfer upon binding to an electron acceptor, C_{60}Py_2 via a two-point binding approach, as shown in Fig. 32 [117].

To establish the energy and electron transfer processes, steady-state absorption and emission studies were performed. The absorption spectrum of the triad showed characteristic peaks of ZnP and ZnPc located at 425 (Soret band) and 685 nm (Q band), respectively, with the absorption peak intensity ratio of 2:1 based on the number of ZnP and ZnPc species of the triad. The fluorescence study was performed upon selective excitation of the ZnP moiety which revealed quenching of characteristic emission bands of ZnP accompanied by the appearance of a band located at 695 nm corresponding to the emission from ZnPc suggesting the occurrence of energy transfer from $^1\text{ZnP}^*$ to ZnPc. Next, the supramolecular tetrad was built by complexing C_{60}Py_2 to $\text{ZnP}_2\text{-ZnPc}$ via the two-point binding methodology. The absorption and emission properties of the complex were then studied. As shown in Fig. 33a, after the addition of C_{60}Py_2 to the solution of the triad, diminished absorption peak intensities accompanied by a red-shift of both ZnP and ZnPc moieties was observed suggesting the formation of a complex via metal-ligand axial coordination. The fluorescence titration was also performed and studied by selective excitation of the ZnP and ZnPc moieties from the triad after the addition of C_{60}Py_2 . This experiment revealed more than 90% quenching of the emission intensity, as shown in Fig. 33e. The optical data were used to calculate the binding constant and mole ratio of the system

which were found as $1.2 \times 10^5 \text{ M}^{-1}$ and 1:1 stoichiometry, respectively. From the structure of the triad and binding site of C_{60}Py_2 in the supramolecular complex, the two geometries were arrived. The first geometry involved axial coordination of C_{60}Py_2 to two Zn metal centers of ZnP while in a second geometry one metal center was from ZnP and another is from ZnPc . By systematic analyses of the optical, computational, and electrochemical experiments results, it was concluded that both ZnP and ZnPc entities were involved to form a tetrad upon coordination of C_{60}Py_2 as shown in Fig. 32.

Fig. 32. Supramolecular tetrad featuring $\text{ZnP}_2\text{-ZnPc}$ axially coordinated with C_{60}Py_2 showing two different possibilities of axial coordination. (adapted from Ref. 117).

The occurrence of photoinduced electron transfer in the complex was investigated by using transient absorption spectroscopy. The supramolecular complex formed by the addition of C_{60}Py_2 to the solution of $\text{ZnP}_2\text{-ZnPc}$ revealed two electron transfer products, $\text{ZnP}_2^{\cdot+}\text{-ZnPc:C}_{60}\text{Py}_2^{\cdot-}$ and $\text{ZnP}_2\text{-ZnPc}^{\cdot+}\text{:C}_{60}\text{Py}_2^{\cdot-}$ species in both DCB and toluene solvents. By monitoring the transient spectral changes and energy level diagram of the system, the stable charge-

separated state was $\text{ZnPc}^{\cdot+}:\text{C}_{60}\text{Py}_2^{\cdot-}$ involving ZnPc and C_{60} . Upon excitation of the complex by using a 400 nm femtosecond laser, two characteristic, pronounced transient peaks were observed located at 850 and 1020 nm which corresponded to the oxidized and reduced forms of ZnPc and C_{60} entities in the supramolecular tetrad. Fast charge separation and slow charge recombination processes were observed in both DCB and toluene with the rate constants of $k_{\text{CS}} = 6.82 \times 10^{11}$ and $2.22 \times 10^{11} \text{ s}^{-1}$ and $k_{\text{CR}} = 1.2 \times 10^9$ and $6.2 \times 10^8 \text{ s}^{-1}$, respectively, thus making the supramolecular complex to be a suitable light energy harvesting system.

Fig. 33. (a) Absorption spectral changes observed during C_{60}Py_2 binding to (ZnP-ZnP)-ZnPc in DCB, (b) Mole ratio plot constructed to evaluate the molecular stoichiometry (425 nm band intensity was used). (c) Benesi-Hildebrand plot to calculate the binding constant. (d) Fluorescence spectrum ($\lambda_{\text{ex}} = 425 \text{ nm}$) of (i) (ZnP-ZnP)-ZnPc triad and (ii) a mixture of ZnP and ZnPc in DCB. The * is due to ZnPc absorbance at this wavelength. (e) Fluorescence spectra of (i) (ZnP-ZnP)-ZnPc triad on increasing addition of C_{60}Py_2 (0.1 eq. each addition) in DCB. $\lambda_{\text{ex}} = 411 \text{ nm}$ corresponding to one of the isosbestic points. (reproduced with permission from Ref. 117).

2.4 Donor-acceptor conjugates having high potential donors

Recently, supramolecular donor-acceptor systems possessing high oxidation potential photosensitizers have gained considerable interest primarily due to the possibility of generating high energy charge-separated states suitable for the development of water oxidation/proton reduction catalysts [118-120]. In this context, a series of high potential metallated porphyrins and phthalocyanines have been designed to study the photoinduced electron transfer processes. Supramolecular dyads comprised of high potential zinc porphyrins and zinc phthalocyanines having various numbers of electron withdrawing halogen atoms, such as fluorine and chlorine, at the periphery in conjunction with coordinated C_{60} Im have been investigated [121-122]. The oxidation of the metalloporphyrins and metallophthalocyanines was harder due to the presence of halogen atoms at the ring periphery that ultimately involved in generating high energy charge-separated states in the dyads.

Das et.al. [121] reported donor-acceptor systems comprised of high oxidation potential ZnPs and C_{60} functionalized with imidazole and pyridine groups, self-assembled via metal-ligand axial coordination. Four derivatives of zinc metallated high potential porphyrins were utilized in this study whose structures are shown in Fig. 34.

Fig. 34. Structure of halogenated ZnPs and C_{60} Im and C_{60} Py. (adapted from Ref. 121).

The optical absorption properties of all four porphyrins were investigated in DCB and compared with tetraphenylporphyrinato zinc (ZnTPP), a control compound. By comparing the

position of the typical Soret band of ZnTPP, which appeared at 419 nm, perturbation in the location of the Soret as well as the visible band was observed due to the presence of halogen atoms at the *meso*-aryl positions of ZnPs. The Soret band of compounds, (Cl₄TPP)Zn, (F₂₀TPP)Zn, (F₄TPP)Zn, and ((CF₃)₄TPP)Zn were at 421, 415, 418, and 418 nm, respectively. Fluorescence study of the high potential ZnPs was also investigated in DCM, which revealed a decrease in quantum yield (up to 40%) along with a change in the position of fluorescence peak maxima. The most diminished fluorescence was observed for (Cl₄ZnTPP) due to heavy atom quenching effects.

The formation of supramolecular dyads between high potential ZnPs with C₆₀Im or C₆₀Py via metal-ligand axial coordination was investigated in DCM. The titration of C₆₀Im and C₆₀Py to the solution of ZnPs revealed changes in absorption spectral characteristics attributed to metal-ligand axial coordination. A Job's plot revealed the ratio of substrate and analyte as 1:1. The formation constant for all the complexes was evaluated by constructing Benesi-Hildebrand plots using absorption spectral data. As expected, the binding constant for C₆₀Im binding to ZnP was higher than that of C₆₀Py binding to ZnP. The calculated binding constants also revealed that the porphyrin macrocycle with increased number of electron withdrawing halogen substituents bind strongly with fullerene ligands. Hence, the *K* values followed the order: (F₂₀TPP)Zn > ((CF₃)₄TPP)Zn > (F₄TPP)Zn > (Cl₄TPP)Zn > ZnTPP. Similarly, fluorescence titrations were also performed by the addition of fullerene ligands to the solution of halogenated ZnPs, which revealed fluorescence quenching during the course of titration. Further, electrochemical studies involving the halogenated ZnPs and fullerene ligands were performed in DCM containing 0.1M of (*t*-Bu₄N)ClO₄ as the supporting electrolyte to gather the redox potential information. Subsequently, the redox and spectral data were utilized to construct an energy level diagram and to calculate the free energy change for electron transfer processes. The redox potentials, upon coordination of C₆₀Im to the halogenated ZnPs, revealed slight shifts indicating some electronic interactions between donor and acceptor entities in the dyad. However, such shifts were nominal for C₆₀Py binding.

Femtosecond transient absorption spectral studies were performed to gather evidence of formation of charge-separated states upon photoexcitation of the dyad and further to

calculate the kinetics of charge separation and recombination processes. The supramolecular dyads were excited using 400 nm laser light that selectively excited ZnP in deaerated toluene solution (see Fig. 35).

Upon excitation of the dyads, characteristic bands at 1000 nm corresponding to fullerene radical anion and a broad band at 630 – 725 nm corresponding to oxidized form of ZnP was clearly observed, as the components of charge-separated states. By monitoring the time profile of

Fig. 35. Femtosecond transient absorption spectra of the dyads in toluene: (a) $(F_{20}TPP)Zn:ImC_{60}$, (b) $((CF_3)_4TPP)Zn:PyC_{60}$, (c) $(Cl_4TPP)Zn:ImC_{60}$, and (d) $(TPP)Zn:ImC_{60}$. The sample were excited with 400 nm wavelength of light. The Figure insets show the time profile of 1000 nm band corresponds to $C_{60}^{\bullet-}$ radical anion. (reproduced with permission from Ref. 121).

Table 3. Rate constants for charge of separation (k_{CS}) and charge recombination (k_{CR}) evaluated by analyzing the time profiles of $C_{60}^{\bullet-}$ band at 1000 nm (from 121).

Donor	Acceptor	k_{CS}, s^{-1}	k_{CR}, s^{-1}	k_{CS}/k_{CR}	τ_{CR}, ps
(F ₂₀ TPP)Zn	C ₆₀ Im	3.8×10^{10}	8.0×10^8	48	1250
	C ₆₀ Py	5.0×10^{10}	10.2×10^8	49	980
((CF ₃) ₄ TPP)Zn	C ₆₀ Im	2.1×10^{10}	6.2×10^8	34	1610
	C ₆₀ Py	2.6×10^{10}	9.2×10^8	28	1090
(F ₄ TPP)Zn	C ₆₀ Im	1.4×10^{10}	4.7×10^8	30	2150
	C ₆₀ Py	1.5×10^{10}	8.9×10^8	17	1115
(Cl ₄ TPP)Zn	C ₆₀ Im	9.8×10^9	3.7×10^8	26	2700
	C ₆₀ Py	1.1×10^{10}	6.9×10^8	16	1459
(TPP)Zn	C ₆₀ Im	5.7×10^9	2.5×10^8	24	4000
	C ₆₀ Py	7.9×10^9	3.8×10^8	21	2600

fullerene radical anion peak at 1000 nm, fast charge separation and relatively slow charge recombination were witnessed, as shown by the data in Table 3. The rate constant of charge recombination was found to follow order: (TPP)Zn < (Cl₄TPP)Zn < (F₄TPP)Zn < ((CF₃)₄TPP)Zn < (F₂₀TPP)Zn. Importantly, the high oxidation potential halogenated porphyrins yielded high-energy radical ion-pairs (1.5-1.9 eV) needed to build energetically capable photo catalytic systems.

Further, the same authors, constructed supramolecular donor-acceptor systems comprised of high potential fluorinated ZnPcs as a donor and C₆₀ functionalized with imidazole and pyridine as acceptor (Fig. 36) to generate energetic radical ion-pairs [122]. Two derivatives of halogenated Pcs, that is, ZnF₁₆Pc and ZnF₈Pc where 16 and 8 F-atoms were directly attached on the periphery of ZnPc macrocycle were utilized in this study.

Fig. 36. Structure of high oxidation potential fluorinated ZnPcs used to build donor-acceptor dyads with C₆₀. (adapted from Ref. 122).

The absorption spectrum of halogenated ZnPcs were recorded in DCB which revealed ZnPc absorption with significantly red-shifted Q-band appearing in the near-IR region. The Q-bands of ZnPc (control compound), ZnF₈Pc and ZnF₁₆Pc were located at 680, 710 and 730 nm respectively. The fluorescence study of halogenated ZnPcs revealed diminished emission intensity with the increase in number of fluorine atoms. The emission peak maxima of ZnPc, ZnF₈Pc and ZnF₁₆Pc were located at 692, 727 and 745 nm, respectively. The quantum yield of ZnF₈Pc and ZnF₁₆Pc was reduced by 30 and 63%, respectively, as compared with the quantum yield of ZnPc used as a control compound. The red-shifted absorption and emission properties of halogenated ZnPcs suggested their significance in harvesting light energy from near-IR portion of electromagnetic spectrum. Both absorption and fluorescence titrations in DCB were performed during the binding of halogenated ZnPcs and fullerene functionalized with N-ligands to establish the formation of donor-acceptor supramolecular dyads via metal ligand axial coordination. Addition of C₆₀Im or C₆₀Py to the solution of ZnPcs revealed characteristic spectral changes along with isosbestic points confirming the formation of donor-acceptor complexes. Job's plots were constructed which confirmed a 1:1 mole ratio between substrate and analyte. Benesi-Hildebrand plots were constructed to calculate the formation constant *K*. The measured *K* values for ZnF₈Pc and ZnF₁₆Pc binding to either C₆₀Im or C₆₀Py were an order of magnitude higher compared with non-halogenated ZnPc binding to these derivatives. The *K* values followed the trend: ZnF₁₆Pc > ZnF₈Pc > ZnPc for given C₆₀ derivatives whereas C₆₀Im had higher values than C₆₀Py. Further, to confirm the formation of the complexes, fluorescence titrations were performed in DCB. Upon addition of C₆₀ ligands to the solution of halogenated ZnPcs, significant quenching of fluorescence intensity was observed indicating the formation of the complex and the occurrence of excited state events. Electrochemical studies were also performed to evaluate the redox potentials of supramolecular dyads and the data was further used to draw the energy level diagram as well as to calculate energetics of charge-separated

ion-pairs. It was found that the fluorinated ZnPcs lower ΔG_{CS} in the order of $ZnPc > ZnF_8Pc > ZnF_{16}Pc$ while an opposite trend was observed for ΔG_{CR} values.

To establish the formation of charge-separated states in these supramolecular donor-acceptor systems, femtosecond transient absorption studies were performed in toluene. Representative spectral data is shown in Fig. 37. Upon excitation, both $ZnPc:C_{60}Im$ and $ZnPc:C_{60}Py$ revealed transient peaks at 848 and 1020 nm characteristic of $ZnPc^{\cdot+}$ and $C_{60}^{\cdot-}$ radicals. Similar characteristic transient peaks corresponding to cation and radical anion ion-pairs were obtained upon excitation for other investigated dyads. Kinetic analysis of the spectral data revealed fast charge separation resulting into the formation of high energy charge-separated states (Table 4). [122]

Fig. 37. Femtosecond transient absorption spectra of (a) $C_{60}Py:ZnF_8Pc$, (b) $C_{60}Im:ZnF_8Pc$ dyads at an excited wavelength 400 nm in nitrogen saturated toluene. The time profile of $C_{60}^{\cdot-}$ and $ZnF_8Pc^{\cdot+}$ at 1020 and 893 nm were shown in Figures c and d. (reproduced with permission from Ref. 122).

Table 4. Rate constants for charge separation (k_{CS}), and charge recombination (k_{CR}) calculated for the various supramolecular dyad system of Zn-phthalocyanine with fullerene derivatives in toluene.

Donor	Acceptor	τ_{CS} (ps)	k_{CS} (s^{-1})	τ_{CR} (ps)	k_{CR} (s^{-1})	k_{CS}/k_{CR}
ZnPc	C ₆₀ Py	75	13.3×10^9	2507	4.0×10^8	33
	C ₆₀ Im	200	5.0×10^9	4800	2.08×10^8	24
ZnF ₈ Pc	C ₆₀ Py	20	50×10^9	1262	7.9×10^8	63
	C ₆₀ Im	52	19×10^9	1568	6.4×10^8	30
ZnF ₁₆ Pc	C ₆₀ Py	11	90×10^9	822	12.1×10^8	74
	C ₆₀ Im	21	47×10^9	980	10.2×10^8	46

2.5 Non-fullerene electron acceptor based donor-acceptor systems

AzaBODIPY Functionalized Pyridine/Imidazole Derivatives for Metal-Ligand Axial Coordination: In the previous examples, we discussed various biomimetic model compounds designed to probe light induced energy and electron transfer events. In these systems, C₆₀ derivatives were chosen as elegant electron acceptor entities due to their unique photophysical and redox properties. A literature survey shows that in the case of electron transfer model compounds, several other electron acceptors including quinone, methyl viologen, and perylene diimide have also been employed [91]. In recent years, because of its high absorptivity in the near-IR region and relatively high fluorescence quantum yield, utilization of BF₂-chelated azadipyrrromethane (azaBODIPY or ADP) in building model systems has generated increased attention [123-124]. Electrochemical studies have revealed facile reduction of azaBODIPY compared to commonly used electron acceptors such as quinones and fullerenes. These properties of azaBODIPY provide unique opportunities to design light energy harvesting model systems. Bandi et.al. [125] recently utilized the near-IR absorbing and emitting azaBODIPY to design donor-acceptor systems via metal-ligand axial coordination. In this study, azaBODIPY functionalized with pyridine or imidazole groups was used as an energy or electron acceptor while zinc phthalocyanine or naphthalocyanine was used as an energy or electron donor. Structure of these compounds is shown in Fig. 38.

The synthesis of bispyridyl or bisphenylimidazolyl azaBODIPY derivatives was achieved by esterification reaction catalyzed by EDCI between bis(hydroxyphenyl) azaBODIPY and carboxy pyridine or 4-carboxyphenylimidazole groups. The absorption spectra of both bis(pyridyl) azaBODIPY (Py₂-azaBODIPY) and bis(phenylimidazolyl) azaBODIPY (Im₂-azaBODIPY) were collected in toluene which revealed a strong absorption at 662 nm and two additional less intense bands at 481 and 315 nm. Similarly, the donors, ZnPc and ZnNc, showed a Q band absorption at 676 and 767 nm, respectively. The emission spectrum of all the studied compounds was also recorded in the same solvent and found with emission maxima peaks at 700, 691, and 780 nm corresponding to Im₂-azaBODIPY, ZnPc, and ZnNc, respectively. The formation of a supramolecular complex between Im₂/Py₂-azaBODIPY and ZnPc/ZnNc via metal-ligand axial coordination was first studied by absorption and emission titration methods in toluene. The difference absorption titration spectra was collected by the addition of equal amounts of known concentration of Im₂/Py₂-azaBODIPY solution to ZnPc or ZnNc and to the reference cell. This was necessary to isolate the spectral changes as both donor and acceptor entities had strong absorption in the spectral region. The characteristic absorption spectral changes upon formation of a complex via metal-ligand axial coordination was observed which was later used to calculate the binding constant of the system by using the Benesi-Hildebrand method. By using the slope and intercept of the linear plot obtained from this method the association constant, K , was evaluated to be 7.8×10^4 , 1.3×10^5 , 2.2×10^4 , $2.3 \times 10^5 \text{ M}^{-1}$ for the formation of Py₂-azaBODIPY:ZnPc₂, Im₂-azaBODIPY:ZnPc₂, Py₂-azaBODIPY:ZnNc₂, and Im₂-azaBODIPY:ZnNc₂, respectively. As expected, due to the stronger ligation effect of the imidazole group compared with pyridine, the complex formed by Im₂-azaBODIPY revealed an order of magnitude higher binding constant than Py₂-azaBODIPY. To calculate the molar ratio of the complexes between Im₂/Py₂-azaBODIPY and ZnPc or ZnNc, ¹H NMR titration was performed which revealed the 1:2 ratio of coordinating ligand to the zinc macrocycles.

Fig. 38. Structure of $\text{Py}_2/\text{Im}_2\text{-azaBODIPY}$, ZnPc and ZnNc . (adapted from Ref. 125).

The fluorescence of ZnPc and ZnNc after addition of $\text{Im}_2/\text{Py}_2\text{-azaBODIPY}$ was also monitored. These experiments revealed drastic fluorescence quenching of ZnPc and ZnNc upon addition of $\text{Im}_2/\text{Py}_2\text{-azaBODIPY}$ ligand likely due to an electron transfer process. To get insight into the geometry and electronic structure, all four supramolecular complexes were optimized by using B3LYP/3-21G(*) method. These optimized structures revealed the azaBODIPY entity to be slightly puckered while the zinc atom in ZnPc and ZnNc were slightly out of the plane due to axial coordination. The frontier orbital calculations revealed HOMO and LUMO orbitals to be located over the zinc macrocycles and azaBODIPY entities, respectively.

To calculate the free energy change for the photoinduced electron transfer process, the redox potentials of individual components as well as the supramolecular complexes were recorded by using a differential pulse voltammetry (DPV) technique in DCB containing 0.1 M $\text{TBA}(\text{ClO})_4$ as a supporting electrolyte. The $\text{Py}_2\text{-azaBODIPY}$ and $\text{Im}_2\text{-azaBODIPY}$ revealed two one-electron reductions at -0.36, -1.12, and -0.39, -1.16 V vs Ag/AgCl , respectively, while the oxidation peaks were located at 1.23 and 1.25 V vs Ag/AgCl , respectively. Similarly, the first oxidation and reduction peaks for ZnPc and ZnNc were located at 0.37, 0.14 and -1.19, -1.29,

respectively. Upon the addition $\text{Py}_2/\text{Im}_2\text{-azaBODIPY}$ into the solution of ZnPc or ZnNc , an anodic shift of oxidation peak of ZnPc by 100 mV and for ZnNc by 80 mV as a result of metal-ligand binding was observed. Finally, femtosecond transient absorption spectral studies were performed to investigate the photodynamics of electron transfer processes within the supramolecular complexes. Upon excitation of the ZnPc or ZnNc in the donor-acceptor systems, photoinduced electron transfer process occurred from $^1\text{ZnPc}^*$ or $^1\text{ZnNc}^*$, formed either by direct excitation or product of energy transfer from $^1\text{azaBODIPY}^*$, to the electron deficient azaBODIPY to produce $(\text{ZnPc})(\text{ZnPc})^{\cdot+}:\text{Im}_2\text{-azaBODIPY}^{\cdot-}$ or $(\text{ZnNc})(\text{ZnNc})^{\cdot+}:\text{Im}_2\text{-azaBODIPY}^{\cdot-}$ charge-separated products. Similar charge-separated states were obtained with the $\text{Py}_2\text{-azaBODIPY}$ ligand system. The rate constants of charge separation and recombination along with its lifetime for all complexes were calculated, as listed in Table 5.

Table 5. Kinetic values of photoinduced charge separation and charge recombination in azaBODIPY-ZnPc and azaBODIPY:ZnNc conjugates in toluene (from Ref. 125).

Conjugate	$k_{\text{CS}}^{\text{S}} / \text{s}^{-1}$	$k_{\text{CR}} / \text{s}^{-1}$	$k_{\text{CS}}^{\text{S}} / k_{\text{CR}}$
$(\text{ZnPc})_2:\text{Py}_2\text{-azaBODIPY}$	8.0×10^{10}	4.4×10^8	180
$(\text{ZnPc})_2:\text{Im}_2\text{-azaBODIPY}$	5.0×10^9	4.0×10^8	13
$(\text{ZnNc})_2:\text{Py}_2\text{-azaBODIPY}$	1.1×10^{11}	8.4×10^8	130
$(\text{ZnNc})_2:\text{Im}_2\text{-azaBODIPY}$	7.7×10^9	5.8×10^8	13

Subphthalocyanine – Naphthalocyanine Conjugate via Metal-Ligand Axial Coordination: El-Khouly et. al. have designed a subphthalocyanine functionalized with a pyridine group at the axial position and used as an electron acceptor after coupling with electron donor, zinc naphthalocyanine via metal-ligand axial coordination, as shown in the Fig. 39 [126]. The purpose of choosing naphthalocyanine as a donor is due to its strong absorption in the visible to near-IR region, solubility in various organic solvents, and an intense radical cation absorption band in the near-IR region serving as clear evidence for light induced charge separation process. Main reasons to choose SubPc as an electron acceptor was its strong absorption in the visible

region, relatively low reorganization energy, and higher energy of excited singlet state (2.16 eV) and triplet excited state (1.40 eV). The absorption spectrum of ZnNc was recorded in DCB which revealed a main absorption band at 779 nm along with some other weak bands at 738, 692, 424, and 350 nm. Similarly, PySubPc revealed a main absorption band at 562 nm along with other weak bands at 517 and 308 nm in the same solvent. The absorption titration experiment was performed by the addition of PySubPc to the solution of ZnNc to visualize the formation of the supramolecular complex. The binding of ZnNc to PySubPc was characterized by monitoring the diminishing intensity of the 779 nm band with a 2 – 4 nm blue-shift. The binding constant of the system was evaluated by monitoring the absorption data using the Benesi-Hildebrand method which was found as $1.2 \times 10^5 \text{ M}^{-1}$ suggesting stable complex formation. In the fluorescence titration, following the addition of PySubPc to ZnNc in argon saturated DCB solution, fluorescence quenching from ZnNc band located at 781 nm accompanied by a 3 nm blue-shift was observed, most probably due to the occurrence of an electron transfer process from the singlet excited state of ZnNc to SubPc. Later a Stern-Volmer plot for quenching of ZnNc from PySubPc was constructed to evaluate the quenching constant K_{sv} which was found as $2.4 \times 10^4 \text{ M}^{-1}$. This revealed the occurrence of an efficient quenching process with the quenching rate constant (k_q) of $1 \times 10^{13} \text{ M}^{-1} \text{ s}^{-1}$.

Fig. 39. Structure of ZnNc, SubPc(Py), and the donor-acceptor complex formed using these entities. (adapted from Ref. 126).

The molecular geometry and electronic structure were arrived by optimizing the complex using the DFT method at the B3LYP/6-311G level. In the optimized structure, the

distance between Zn:N from the axial coordination bond was 2.126 Å. The frontier orbitals, HOMO and LUMO, were located on ZnNc and SubPc(Py), respectively. The redox potentials of SubPc(Py):ZnNc were measured in dichloromethane containing (TBA)ClO₄. The DPV of the complex revealed the first oxidation and reduction processes to occur at 0.60 and -1.03 V vs SCE corresponding to ZnNc and SubPc(Py), respectively. From these redox potential values, the free energy change for photoinduced charge separation was calculated for events occurring from both ¹ZnNc* and ¹SubPc* and found as -0.15 and -0.61 eV, respectively, indicating the occurrence of exothermic photoinduced electron transfer processes irrespective of the excited sensitizer.

Femtosecond transient absorption spectra were recorded to characterize the charge-separated states of the complex SubPc(Py):ZnNc in DCB by using a 430 nm wavelength of light. Upon excitation, a clear band located at 956 nm corresponding to the radical cation of ZnNc^{•+} was observed within 10 – 200 ps, as shown in Fig. 40. The rate constant of charge separation and recombination was calculated by monitoring the decay profile of the radical cation band of ZnNc^{•+} and found as 1.30x10¹⁰ s⁻¹ and 1x10⁹ s⁻¹, respectively, with the lifetime of the charge-separated state of nearly 1 ns.

Fig. 40. Femtosecond transient absorption spectra of SubPc(Py):ZnNc dyad in deaerated DCB excited at 430 nm. The figure insets shows the decay profile of ZnNc^+ radical cation. (reproduced with permission from Ref. 126).

2.6 Supramolecular triads assembled in perpendicular fashion

A series of porphyrin based donor-acceptor conjugates were recently constructed and used to study the pathways of electron transfer processes where the arrangement of various components were in perpendicular orientation to the porphyrin plane. The employed aluminum porphyrin in this study was unique and synthetically more advantageous as it provided a reaction site on both faces of the porphyrin plane. The axial hydroxyl group on one side of the Al(III) porphyrin plane was able to form a covalent ester or ether bond while Lewis bases such as pyridine or an imidazole group formed a metal-ligand axial coordination on other side of the plane. The advantage over the configuration of the conjugate is that the donor and acceptor sides of the complex are located on opposite faces of the porphyrin which minimizes the rate of charge recombination. Moreover, the excited state π^* orbital of porphyrin and axially coordinated ligand lay in the same space which causes an increase in the electronic coupling thus facilitating the electron transfer process. Puddotoori et. al. assembled such supramolecular donor-acceptor systems consisting of Al(III)Por with axially bounded naphthalenediimide (NDI) and tetrathiafulvalene (TTF) as acceptor and donor, respectively (**Fig. 41**) [127].

The AlPor allowed two different groups to attach at the opposite faces of AlPor. In the triad, the NDI and TTF groups were attached on the opposite faces of the AlPor via covalent bonding and a metal-ligand coordination bond, respectively. The primary electron transfer occurred from the singlet excited AlPor to NDI followed by a hole shift from oxidized AlPor to axially coordinated TTF, which was confirmed by various spectroscopic techniques. The absorption spectrum of covalently linked AlPor-NDI dyad in dichloromethane revealed a typical porphyrin Soret band at 415 nm and a Q band at 547 nm while the absorption from NDI revealed bands located at 342, 360, and 382 nm. The fluorescence study of the same dyad in DCM and benzonitrile was also recorded through excitation at 550 nm which revealed fluorescence quenching of the dyad in both solvents. Since there was no evidence of spectral

overlap between these two entities, the energy transfer quenching process between them was ruled out. On the other hand, from the redox data, it was revealed that the electron transfer species of the dyad $\text{AlPor}^{\bullet+}\text{-NDI}^{\bullet-}$ lays energetically below compared with $^1\text{AlPor}^*$ in both solvents. The free energy change for charge separation (ΔG_{cs}) was -0.86 and -0.91 eV in DCM and benzonitrile, respectively. Consequently, the electron transfer process from $^1\text{AlPor}^*$ to NDI was the most likely quenching process in the dyad. To get insight into the formation of the supramolecular complex, the absorption titration between AlPor-NDI and Py-TTF in DCM was performed. Upon the addition of Py-TTF, the Q-band of porphyrin was shifted from 546 and 585 nm to 562 and 602 nm along with an isosbestic point located at 555 nm indicating the formation of the complex. A Benesi-Hildebrand plot was constructed to calculate the formation constant of the complex which was $K = 1.1 \times 10^3 \text{ M}^{-1}$. The electronic structure of the self-assembled triad, TTFPy:AlP-NDI, from computational studies revealed the HOMO, HOMO-1, and LUMO located on the TTF, AlP, and NDI units, respectively. Thus the excitation of porphyrin transfers an electron to the LUMO on NDI followed by a hole shift to the HOMO on TTF.

Fig. 41. Structure of TTF:AlPor-NDI supramolecular triad. (adapted from Ref. 127).

Transient absorption spectra of the complex was recorded in DCM and benzonitrile solvents saturated with argon using a 532 nm laser. In the nanosecond transient absorption regime, upon excitation of the dyad, AlPor-NDI, a transient peak located at 470 nm corresponding to $^3\text{AlPor}^*$ with the lifetime of 17 μs was observed. From the energy level diagram, the electron transfer process was possible from both the singlet and triplet excited states of AlPor. However, additional transient bands corresponding to formation of the charge-separated state in the dyad as $\text{AlPor}^{+\bullet}\text{-NDI}^{-\bullet}$ radical ions were not observed because of its shorter lifetime compared with the instrument's dynamic range. When the triad TTF-Py:AlPor- C_{60} was excited, no clear evidence of a charge-separated state was observed because of the shorter lifetime of the charge-separated state. Later, a spin polarized transient EPR spectrum of the complex was recorded which revealed the coupling of an initial charge-separated state between $\text{TTF}^{+\bullet}\text{-NDI}^{-\bullet}$ ion-pairs. The initial polarization experiment revealed the occurrence of an initial charge-separated state which took place from the singlet channel and then singlet-triplet mixing occurred in the primary radical pair. The singlet and triplet lifetime of $\text{TTF}^{+\bullet}\text{-NDI}^{-\bullet}$ radical ion-pair was calculated to be 200-300 ns and 10 μs , respectively.

To further study the sequential energy and electron transfer process, a dyad consisting of Al(III)Por covalently connected via an ester linkage to a free-base porphyrin with electron withdrawing halogen atoms at the *meso* positions was synthesized. On the other side of the Al porphyrin, a pyridine appended TTF derivative was axially coordinated to the central Al atom of AlPor to form a self-assembled donor-acceptor supramolecular triad complex (see Fig. 42 for structure) [128].

The free-base porphyrin with electron withdrawing fluorine atoms at *meso* positions was selected as an acceptor for both energy and electron transfer processes because of its spectral overlapping with AlPor and positive redox potentials suitable for an electron acceptor. At the same time tetrathiafulvalene (TTF) was selected as a secondary donor because of its strong electron donating ability. The absorption spectrum of the dyad Al(III)Por- H_2P was recorded in DCM, which revealed three Q bands located at 510, 547, and 639 nm corresponding to H_2Por (87%), AlPor (90%), and H_2Por (60%), respectively. Steady-state fluorescence was measured in the same solvent by exciting the dyad at 550 nm; i.e. the absorption of AlPor

revealed 90% fluorescence quenching because of the singlet-singlet energy transfer from AlPor to H₂Por. To investigate the formation of a complex, both absorption and fluorescence titrations were performed by the addition of TTFPy into a solution of dyad in DCM. Upon addition of TTFPy, the Q bands from the porphyrin shifted from 547 and 586 nm to 563 and 603 nm, respectively, along with the appearance of an isosbestic point at 555 nm which indicated the formation of the triad TTF-Py:AlPor-H₂Por via metal-ligand axial coordination. A Benesi-Hildebrand plot was constructed which revealed the formation of 1:1 complex with binding constant $K = 1.8 \times 10^3 \text{ M}^{-1}$. A similar binding constant was obtained upon the titration of TTF-Ph-Py ligand ($K = 2.0 \times 10^3 \text{ M}^{-1}$). Further, the steady-state fluorescence titration was performed by the addition of TTFPy into the solution of the dyad, which revealed the fluorescence band of AlPor from the dyad shifted to longer wavelength along with significant fluorescence quenching because of sequential energy transfer from AlPor to H₂Por followed by an electron transfer process from TTF to AlPor in the complex. All these photoactive events were later studied and confirmed by femtosecond transient absorption spectroscopy.

Femtosecond transient absorption spectroscopic studies were performed to investigate the energy and electron transfer events in the dyad, AlPor-H₂Por. A complex transient spectra was obtained with negative peaks located at 509, 545, 645, and 716 nm and positive peaks located at 448, 528, 565, 618, 671, 1064, and 1240 nm. By monitoring the singlet peak at 1024 nm of ¹H₂Por*, which stays longer after the depletion of the peak at 1240 nm of ¹AlPor*, occurrence of energy transfer in the dyad from ¹AlPor* to H₂Por was established. The rate constant of energy transfer in the dyad was calculated as $k_{\text{ENT}} = 1.78 \times 10^8 \text{ s}^{-1}$. The transient absorption study of the triad by adding TTFPy into the solution of AlPor-H₂Por was investigated in DCB. Upon excitation of the triad, a complex transient spectra of the system was observed in the visible region because of the moderate binding constant between TTF and AlPor-H₂Por dyad and strong spectral absorption of AlPor and H₂Por. However, the formation of TTF^{•+}-AlPor^{•-} radical ion-pairs was confirmed by monitoring the transient peaks located in the 450 – 500 nm and 600 – 650 nm regions, respectively. Hence, in the triads,

Fig. 42. Proposed modulation of photoinduced energy and electron transfer processes in dyads and triads. (adapted from Ref. 128).

photoexcitation of the AlPor produced a fast electron transfer from TTF to AlPor with rate constant of $k_{ET} = 8.33 \times 10^9 - 1.25 \times 10^{10} \text{ s}^{-1}$ to yield a primary radical ion-pair $\text{TTF}^{\bullet+}\text{-AlPor}^{\bullet-}\text{-H}_2\text{Por}$. This process is further followed by an electron shift to produce $\text{TTF}^{\bullet+}\text{-AlPor-H}_2\text{Por}^{\bullet-}$ as a final charge-separated state. Similar results were observed when TTF-Ph-Py coordinating ligand was used. In summary, upon photoexcitation of AlPor-H₂Por in non-coordinating solvent (DCM and DCB), the AlPor moiety served as an antenna system by transferring its excitation energy to H₂Por with rate constant (k_{ENT}) of $1.78 \times 10^8 \text{ s}^{-1}$. In contrast, upon excitation of the AlPor in the triad, TTF-AlPor-H₂Por, sequential electron transfer process between TTF, AlPor, and H₂Por, was observed resulting in $\text{TTF}^{\bullet+}\text{-AlPor-H}_2\text{Por}^{\bullet-}$ as the final charge-separated state. These photochemical events are depicted in **Fig. 42**.

Recently, a triad consisting of Al(III)Por covalently connected to Au(III)Por via ester linkage on one side and axially coordinated with TTF functionalized with imidazole on the other side of Al porphyrin was designed and studied as an light energy harvesting system, as shown in **Fig. 43** [129]

The perpendicular arrangement of the self-assembled system provided an opportunity to study a sequential energy and electron transfer processes where the Al(III)Por acted as a

primary electron donor, while the Au(III)Por and TTF served as an electron acceptor and hole shift agents, respectively. The main reason to select Au(III)Por in this study was the minimum spectral overlap between AlPor and AuPor absorption, positive shift in redox potential, and an increase in the singlet excited state energy suitable for photoinduced electron transfer events. The UV/Visible absorption spectrum of the dyad AlPor-AuPor⁺ was recorded in DCM which revealed peaks at 406 and 520 nm corresponding to AuPor, and peaks at 415 and 550 nm corresponding to AlPor. Fluorescence study of the dyad in the same solvent was conducted by excitation at 550 nm which revealed more than 80% fluorescence quenching likely due to electron transfer process from ¹AlPor* to AuPor. To study the formation of supramolecular self-assembled triad, an absorption titration was performed by the addition of Py-TTF into the solution of AlPor-AuPor in DCM. During the binding process of TTF-Py, the Q band at 549 nm of AlPor was shifted to 560 nm along with an increase in absorbance of 604 nm band. The appearance of isosbestic point at 555 nm further supported the formation of TTF-Py:AlPo-AuPor complex. A Benesi-Hildebrand plot was constructed by monitoring change in absorption which revealed the formation of 1:1 complex with binding constant $K = 3.3 \times 10^3 \text{ M}^{-1}$. Similarly, the binding constant of TTF-Ph-Py:AlPor-AuPor was also calculated and found as $K = 3.5 \times 10^3 \text{ M}^{-1}$. Further, the fluorescence titration was also performed by increasing addition of TTFPy into the solution of AlPo-AuPor dyad which was excited at 555 nm, an isosbestic point obtained from the absorption titration. The quenching of AlPor-AuPor was further increased upon binding of TTFPy because of the presence of a hole transfer agent in the system which also supported the formation of a complex.

Fig. 43.

Structure of vertically arranged self-assembled supramolecular triads *via* metal-ligand axial coordination. (adapted from Ref. 129).

To secure the evidence of electron and hole transfer processes within the triad, femtosecond transient absorption spectral study was performed in DCB by using 400 nm light. Representative data are shown in Fig. 44. First, transient absorption spectra of dyad AlPor-AuPor was recorded which revealed two clear transient peaks at 612 and 655 nm corresponding to the formation of AlPor^{•+} and AuPor^{•-} cation and radical anion peaks, respectively; evidence for an initial charge separation process. By global fitting of time profile of the 612 nm peak, the rate constants of charge separation (k_{CS}) and charge recombination (k_{CR}) was calculated to be $3.17 \times 10^{11} \text{ s}^{-1}$ and $3.67 \times 10^{10} \text{ s}^{-1}$, respectively. After the coordination of TTFPy to the dyad and upon the excitation, three clear transient peaks were observed at 612, 650, and 412 nm corresponding to AuPor^{•-}, AlPor^{•+}, and TTF^{•+} radical ions, respectively. These results were consistent with both of the coordinating ligands, i.e. TTF-Py and TTF-Ph-Py. By monitoring the 612 nm transient peak which corresponds to AuPor^{•-}, the rate constant of charge separation (k_{CS}) and recombination (k_{CR}) in the triad TTF-Py:AlPor-AuPor were calculated and

found as $5.4 \times 10^{10} \text{ s}^{-1}$ and $7.59 \times 10^8 \text{ s}^{-1}$, respectively. Similarly, by monitoring 612 nm transient peak, the k_{CS} and k_{CR} were found for the triad TTF-Ph-Py:AlPor-AuPor as $1.64 \times 10^{10} \text{ s}^{-1}$ and $6.74 \times 10^8 \text{ s}^{-1}$, respectively.

Fig. 44. Femtosecond transient absorption spectra of (a) TTF-Py:AlPor-Ph-AuPor⁺ (3:1 ratio) (b) TTF-Ph-Py:AlPor-Ph-AuPor⁺ (3:1 ratio) in DCB at the excitation wavelength of 400 nm. Figures e and f represent the time profiles of transient peaks of TTF-Py:AlPor-Ph-AuPor⁺ and TTF-Ph-Py:AlPor-Ph-AuPor⁺, respectively. (reproduced with permission from Ref. 129).

2.7 Donor-acceptor conjugates assembled via multiple types of binding motifs

X-ray structural studies on various natural light energy harvesting systems have revealed that all of the chromophores within the system involved in energy and electron transfer reactions are held together by non-covalent interactions. In recent years, researchers have made significant progress in designing such non-covalently linked light energy harvesting systems using complementary binding interactions. In few instances, these nanostructures have revealed both specificity and directionality.

Incorporation of multiple non-covalent interactions within supramolecular systems provide higher stability and defined geometry. D'Souza et.al. have assembled a supramolecular tetrad composed of two tetra-crown ether functionalized ZnPc units (ZnTCPc), four potassium ions (K^+), and two fullerene derivatives functionalized with a pyridine and terminal ammonium cation moiety ($pyC_{60}NH_3^+$), as shown in Fig. 45 [130].

Fig. 45. Structure of supramolecular assembly composed of two crown ether appended phthalocyanine, four units of potassium ions, and a fullerene bearing ammonium cation and pyridine. (adapted from Ref. 130).

This system was held together by a combination of multiple interactions. The first one was a cation-crown ether interaction between the four potassium ions and the four crown ethers appended phthalocyanine leading to the formation of co-facial Pc-Pc dimer. The second one was metal-ligand interaction between the central zinc atom of phthalocyanine and the pyridine group from the C_{60} derivative. The stability of the complex was further enhanced by interaction of the terminal ammonium cation attached to the C_{60} derivative with one of the crown ethers of phthalocyanine without destroying the sandwich dimer complex formed by the four potassium ions. Slight increase in the absorption intensity of ZnPc Soret band and

appearance of a new band at 636 nm upon addition of K^+ ion revealed the formation of a cofacial dimer assisted by K^+ ions.

On addition of fullerene functionalized $PyC_{60}NH_3^+$ to the co-facial dimer, $K_4[ZnTCPC]_2$, a decrease in the absorption intensity of the 636 nm band with the appearance of isosbestic points at 627 and 647 nm along with a sharp peak around 432 nm corresponding to fulleropyrrolidine peak was observed. The formation of the complex was further supported by monitoring the fluorescence spectrum of the complex. Addition of K^+ ions into the ZnTCPC solution showed a 90% quenching of fluorescence intensity of phthalocyanine as a consequence of a static quenching. The quenching is further increased to 98% upon addition of $PyC_{60}NH_3^+$ due to the presence of the electron acceptor C_{60} . A cyclic voltammetric study was performed to monitor the change in redox potentials upon the formation of the complex. The pristine ZnTCPC showed the first oxidation and reduction potentials at -0.08 and -1.80 vs Fc/Fc^+ . The splitting of the first oxidation peak from ZnTCPC upon addition of K^+ in the solution indicated the formation of a strong cofacial phthalocyanine dimer. Further, addition of $PyC_{60}NH_3^+$ to the phthalocyanine dimer, a diminished current was observed because of the formation of bulky (difficult to diffuse) supramolecular donor-acceptor conjugate, $K_4[ZnTCPC]_2:(PyC_{60}NH_3^+)_2$.

The kinetics of photoinduced electron transfer in the supramolecular complex was studied by using transient absorption spectroscopy. The transient spectra was recorded first by forming the $ZnTCPC:PyC_{60}NH_3^+$ complex by addition of equimolar ZnTCPC and $PyC_{60}NH_3^+$ in the absence of K^+ ion, which revealed bands at 870 and 1000 nm corresponding to the formation of $ZnTCPC^{\cdot+}$ and $C_{60}^{\cdot-}$, respectively. The rate constant for charge separation and recombination was calculated by monitoring any of these radical ion-pair peaks was $2.1 \times 10^5 \text{ s}^{-1}$ with the lifetime of 4.8 μs for the charge-separated state. The rate constants and the lifetime of charge separation and recombination for the $K_4[ZnTCPC]_2:(PyC_{60}NH_3^+)_2$ complex was monitored which revealed further stabilization of the charge-separated state with the rate constant of $1.5 \times 10^5 \text{ s}^{-1}$ and lifetime of 6.7 μs .

Grimm et.al. [131] have designed a donor-acceptor model system by using two complementary supramolecular motifs, that is, multi-point hydrogen bonding and metal-ligand

axial coordination, which controlled the step-by-step formation of complexes to harvest the light energy efficiently. In this study, supramolecular interaction between perylene diimides and ZnTPP, which were functionalized with a Hamilton receptor and cyanuric acid, respectively, was established via the multi-point H-bonding approach. This interaction left the zinc metal from ZnTPP free for axial ligation, allowing complexation of 4-pyridylfullerene, as shown in Fig. 46.

Fig. 46. Structure and interaction of PDI, ZnP, and PyC₆₀ multi-point bound supramolecular system. (adapted from Ref. 131).

Upon photoexcitation, energy transfer occurred from the singlet excited PDI to the low lying singlet excited state of ZnTPP followed by an electron transfer process from ¹ZnTPP* to the axially coordinated PyC₆₀ to generate charge-separated state, which was later confirmed by using transient spectroscopy.

The absorption spectrum of the individual components of the system was recorded which revealed absorption at different regions of the solar spectrum. PDI absorbed in the visible region with peak maxima at 464, 495, and 532 nm. ZnTPP revealed a characteristic porphyrin absorption in visible region. Fullerene also had a characteristic absorption in the UV and visible region. Fluorescence spectra of all the components was recorded and revealed peak maxima at 544 nm corresponding to PDI, and 600 to 700 nm corresponding to ZnP. To get insight into the formation of a supramolecular complex, both absorption and fluorescence titrations were performed in DCB. The initial absorption titration between PDI and ZnP revealed the spectra with peak maxima at 458, 490, and 526 nm corresponding to PDI, along with peak maxima at 421, 547, and 585 nm corresponding to ZnP. The lack of appreciable change in the

absorption spectra from the titration suggested the absence of ground state interactions between the two entities. A Job's plot was constructed from this experimental data which revealed the formation of a 1:1 complex. In the excited state, on the other hand, the addition of ZnP to PDI solution revealed successive quenching of PDI emission which reached more than 60%. This indicated occurrence of an energy transfer process in the system. The association constant of the system via hydrogen bonding was evaluated to be $9.5 \times 10^5 \text{ M}^{-1}$. In another complementary fluorescence titration, ZnP was titrated with PyC₆₀, a complex was formed via metal-ligand axial coordination and revealed a characteristic quenching of emission from ZnP which exceeded more than 80%. The association constant of the latter system was also evaluated by monitoring the change in fluorescence as $3.4 \times 10^6 \text{ M}^{-1}$ in DCB. Later, absorption titration of all three species was performed where the PyC₆₀ was added to the complex formed earlier by ZnP:PDI, which revealed the appearance of two isosbestic points located at 416 and 431 nm. From this titration a new association constant was evaluated to be $2.7 \times 10^5 \text{ M}^{-1}$, an order of magnitude lower than ZnP:PyC₆₀ via metal-ligand axial coordination. Furthermore, the fluorescence titration of the PDI:ZnP:PyC₆₀ system was also performed which led to substantial quenching of the fluorescence via energy and electron transfer mechanisms.

To further confirm the occurrence of light induced charge separation, transient spectral studies were performed in DCB. Upon excitation with 530 nm light, the transient spectra of PDI revealed negative peaks at 465, 496, and 590 nm corresponding to the ground state depletion and positive peaks at 690, 760, 870, and 940 nm. Similarly, upon excitation of the ZnP by 420 nm light revealed peak minima at 560 and 600 nm and maxima at 458, 583, and 625 nm. Next, the excited states from the complex PDI:ZnP was monitored by using 530 nm light. This revealed the fast decay of singlet PDI excited state with an increase in the excited state transient peaks of ZnP, with peak maxima at 409, 451, and 475 nm and minima at 428 nm with the time scale of 50 – 100 ps. This observation suggested occurrence of an energy transfer process from the ¹PDI* to ZnP via the H-bonding motif. Next, the transient spectra of ZnP:PyC₆₀ was recorded by using 420 nm light. In the early time scale, a maxima and minima at 480 and 560 nm, respectively, was observed which at later delay times, decayed and produced a clear maxima at 494 and 635 nm and another maxima in the near-IR region at 1005 nm. The bands in

the visible region correspond to ZnP^+ and the band in the near-IR region corresponds to the reduced form of C_{60} radical anion. This result suggested the occurrence of an electron transfer process from singlet excited ZnP to PyC_{60} in the $\text{ZnP}:\text{PyC}_{60}$ complex to form a charge-separated state with lifetime of 1 ns. A final transient experiment with the triad $\text{PDI}:\text{ZnP}:\text{PyC}_{60}$ was performed by using 530 nm light. Upon excitation, the instantaneously formed spectra revealed peak minima at 464, 497, 588 nm and maxima at 693, 760, 863, and 941 nm. Later, bands at 421, 475, 630, and 995 nm were observed which confirmed the formation of $\text{ZnP}^+/\text{PyC}_{60}^-$ radical ion-pairs. The lifetime of charge-separated states in the latter complex $\text{PDI}:\text{ZnP}:\text{PyC}_{60}$ was calculated to be 3.8 ns indicating stabilization of charge-separated state of $\text{ZnP}^+/\text{C}_{60}^-$ from 1 ns obtained in the $\text{ZnP}:\text{PyC}_{60}$ complex.

In another elegant study, a supramolecular oligochromophoric system possessing exclusive binding sites for both a guest electron acceptor and an anionic cofactor species was developed, and anion-binding-induced stabilization of charge-separated state was successfully demonstrated [132]. Towards this, intramolecular and intermolecular photochemical processes of a supramolecular complex of a bis-porphyrinyl-substituted oxoporphyrinogen (OxP) with a bis(4-pyridyl)-substituted fullerene (Fig. 47) were investigated by using femtosecond and nanosecond laser flash photolysis measurements. Transient absorption spectra of the supramolecular complex obtained by femtosecond laser flash photolysis indicated efficient electron transfer occurring from the porphyrin moiety to the fullerene moiety, followed by faster back electron transfer to the ground state. Binding of several different anionic species at the pyrrole amine groups of an oxoporphyrinogen unit within the supramolecular complex was found to improve the rate of the photoinduced electron transfer due to the favorable structural changes. The anion binding also improved persistence of the photoinduced charge-separated state between the anion-bound oxoporphyrinogen and fullerene moieties, which was produced by intermolecular electron transfer from the triplet excited state of porphyrin to fullerene as indicated by the nanosecond laser flash photolysis measurements. Upon fluoride anion binding to OxP, anion-complexation-induced stabilization of charge separation gave a 90 fold elongation of the CS state lifetime from 163 ns to 14 μs . Complexation with other anions (acetate or dihydrogenphosphate) also resulted in stabilization of the CS state, whereas weakly

bound perchlorate anions gave no improvement. Complexation of anions to the oxoporphyrinogen center lowered OxP oxidation potential by nearly 600 mV creating an intermediate energy state for charge migration from the $\text{ZnP}^{\bullet+}$ to the oxoporphyrinogen:anion complex. An increase in reorganizational energy of electron transfer combined with the decrease in charge recombination driving force caused by anion binding resulted in an increase in the lifetime of the charge-separated state.

Fig. 47. Structural origin of two-guest reagent/anion cofactor complexation (left figure, peripheral substituents are omitted for clarity) and chemical structure of the *bis*-porphyrin-substituted oxoporphyrinogen and *bis*(4-pyridyl)-substituted fullerene used in this work. Axial coordination and anion binding site are also shown for clarity. (adapted from Ref. 132).

2.8 Endohedral fullerene based donor-acceptor systems

Various donor-acceptor systems have been designed to harvest light energy by generating energetic charge-separated states. Fullerene, as an electron acceptor, possesses remarkable photophysical and photochemical properties and low reorganization energy necessary for photoinduced electron transfer processes, and thus has attracted many researchers in this field. On the other hand, endohedral fullerenes, carbon cage for various species such as atoms, ions, and clusters, displays unique redox chemistry different from empty fullerenes [87-88]. These molecules have gained lot of attention as electron acceptors [87]. The endohedral fullerenes display an improved absorption coefficient in the visible region of the electromagnetic spectrum and reduced HOMO-LUMO gaps when compared with empty fullerenes, which make them an excellent candidates for optoelectronic applications. Because

of the unique photophysical and photochemical properties of endohedral fullerenes, various research groups have attempted designing supramolecular donor-acceptor systems.

Supramolecular donor-acceptor systems via metal-ligand axial coordination, in which endohedral fullerenes functionalized with pyridine group acting as an electron acceptor and zinc porphyrin (ZnP) acting as an electron donor, were designed by Tsuchiro et.al. to study their photophysical and photochemical properties. Structure of the different entities is shown in Fig. 48 [133].

Fig. 48. Structure of endohedral fullerene and ZnP used in building donor-acceptor systems. (adapted from Ref. 133).

Two different endohedral fullerenes encapsulating lanthanum atoms to form lanthanum metallofullerene derivatives, named $La@C_{82}Py$ and $La_2@C_{80}Py$, along with C_{60} as a control compound functionalized with pyridine group were utilized. The endohedral fullerene derivatives were synthesized by using 1,3-dipolar cycloaddition with azomethine ylides reaction popularly known as the Prato reaction [85]. These fullerene derivatives were isolated by HPLC and were characterized by mass spectrometry (MALDI-TOF), EPR, and NMRs (1H and ^{13}C). The formation of a supramolecular complexes via metal-ligand axial coordination were examined using both absorption and fluorescence titrations between pyridine functionalized endohedral fullerenes and ZnP in toluene and chlorobenzene. Upon the addition of fullerene derivatives to a solution of ZnP, the absorption spectra of porphyrin revealed perturbation of the Soret and the Q bands along with the appearance of an isosbestic point. Said changes were characteristics to axial coordination phenomena which suggested the formation of a self-assembled complexes. By utilizing the change in the absorption spectral data, a Job's plot revealed the

formation of a 1:1 complexes. The association constants of the self-assembled systems were calculated by using same spectral data and found as $\log K_{\text{assoc}} = 4.02, 3.95, \text{ and } 4.38$ corresponding to $\text{C}_{60}\text{Py}:\text{ZnP}$, $\text{La}@\text{C}_{82}\text{Py}:\text{ZnP}$, and $\text{La}_2@\text{C}_{80}\text{Py}$, respectively. Steady-state fluorescence titrations of all C_{60}Py derivatives binding to ZnP was also performed in chlorobenzene which revealed the quenching of fluorescence intensity of the ZnP band located at 595 and 645 nm likely due to photoinduced electron transfer from $^1\text{ZnP}^*$ to C_{60} derivatives.

The confirmation of charge-separated states and kinetics of all photochemical events in these complexes were evaluated by performing transient absorption spectroscopy using both femto- and nanosecond regimes. Excitation of only $\text{La}@\text{C}_{82}\text{Py}$, an open shell species, at 387 nm revealed two transient bands located at 570 and 900 nm which rapidly transformed into a band at 780 nm that was a quartet excited state. This quartet excited state was later subjected to ground state recovery within 100 ns. Photoexcitation using 420 nm to selectively excited ZnP in the $\text{La}@\text{C}_{82}\text{Py}:\text{ZnP}$ complex revealed a broad absorption peak located at 950 nm and a negative peak at 1170 nm confirming the formation of $\text{La}_2@\text{C}_{80}\text{Py}^-$. A band in the visible region located at 600-700 nm due to ZnP^+ was also observed. Later, the excitation of $\text{La}_2@\text{C}_{80}\text{Py}$, a closed shell species, by using 387 nm light, revealed a ground state bleaching at 465 nm accompanied by well-defined peaks with maxima at 466, 516, 614, 735, and 900 nm. Upon excitation of the dyad complex $\text{La}_2@\text{C}_{80}\text{Py}:\text{ZnP}$, by using 420 nm pulse of light, transient peaks located in the visible region around 600-700 nm corresponding to ZnP^+ and a broad band maxima at 1215 nm along with weaker minima at 835 and 960 nm corresponding to the formation of $\text{La}_2@\text{C}_{80}\text{Py}^-$ were revealed. The kinetics of charge separation and recombination processes of these complexes were evaluated and were in the range of 10^{10} s^{-1} and 10^8 s^{-1} , respectively.

To gain further insight into the mechanism of photoinduced electron transfer processes in a supramolecular donor-acceptor system, additional endohedral fullerene based electron acceptor comprised conjugates were designed and studied. To achieve such a system, Trukhiuna et. al. have designed a novel donor-acceptor system consisting of $\text{Sc}_3\text{N}@\text{I}_h\text{-C}_{80}\text{Py}$ endohedral fullerene functionalized with a pyridine molecule capable of axially coordinating to electron donating or accepting zinc phthalocyanines in order to study the bidirectional

mechanism of electron transfer process. Structure of employed compounds is shown in Fig. 49 [134].

Fig. 49. Structure of donor-acceptor system formed via metal-ligand axial coordination. For *t*-butylZnPc, R_1 and $R_2 = t$ -butyl and H, respectively, while for $\text{ZnPc}(\text{SO}_2)_8$, R_1 and $R_2 = \text{SO}_2\text{C}_5\text{H}_{11}$. (adapted from Ref. 134).

When $\text{Sc}_3\text{N}@\text{I}_h\text{-C}_{80}\text{Py}$ was coordinated with an electron donating tetra *t*-butyl-ZnPc (*t*-butyl ZnPc), excitation revealed the direction of photoinduced electron transfer process from $^1\text{ZnPc}^*$ to endohedralfullerene. On the other hand, the reverse process was observed when electron withdrawing ZnPc, octakis-(pentylsulfonyl) Zn(II)Pc ($\text{ZnPc}(\text{SO}_2)_8$) was used. To observe the interaction of various donor-acceptor systems via axial coordination, an absorption titration was performed in DCB. Upon the addition of fullerene appended pyridine species into both ZnPc derivative solution, the Soret and Q bands located at 350 and 680 nm of *t*-butyl ZnPc and at 360 and 690 nm of $\text{ZnPc}(\text{SO}_2)_8$ were perturbed along with the concurrent appearance of isosbestic points suggesting the formation of a supramolecular complexes. By monitoring the

spectral changes, a 1:1 stoichiometry for both complexes was arrived. To further observe the change in excited state interactions, a steady-state fluorescence titration was performed in DCB. The ZnPc centered fluorescence of both ZnPc derivatives was monitored after increasing additions of fullerene derivative. Upon excitation at 610 (for *t*-but-ZnPc) and 630 nm (for ZnPc(SO₂)₈), exponential fluorescence quenching of the system due to the formation of the complex was observed. The formation constant of both complexes was calculated by monitoring the fluorescence quenching data which was found as $\log K = 5.5$ and 5.9 for *t*-butZnPc:Py-SC₃N@I_hC₈₀ and ZnPc(SO₂)₈:Py-SC₃N@I_hC₈₀ complexes, respectively.

Later, to get insight into the formation of charge-separated states and kinetics of various transient events, the femtosecond transient spectral studies in argon saturated chlorobenzene, using 676 nm excitation was performed. Upon excitation of *t*-butZnPc:Py-SC₃N@I_hC₈₀, positive transient peaks at 500, 600, 640, 739, and 825 nm while negative transient peaks due to ground state depletion at 615 and 683 were also observed. At a delay time of 6.8 ps, new transient peaks were generated at 440, 512, and 850 nm revealing the formation of ZnPc^{•+}. The peaks of fullerene radical anion was superimposed over the radical cation peak. Thus, the final charge-separated state was established as *t*-butZnPc^{•+}:Py-SC₃N@I_hC₈₀^{•-}. Similarly, upon excitation of the ZnPc(SO₂)₈:Py-SC₃N@I_hC₈₀ complex, positive transient peaks at 522, 647 and 850 nm and negative peaks due to ground state depletion at 624 and 695 nm were observed. At a time delay of 6.6 ps, new transient peaks appeared and were located at 465, 603, 646, 760, and 1060 nm confirming formation of ZnPc^{•-}. On the other hand, the radical cation, located on fullerene, was also detected and confirmed by spectroelectrochemistry. Thus the final charge-separated state was ZnPc(SO₂)₈^{•-}:Py-SC₃N@I_hC₈₀^{•+}. The kinetics of the charge recombination process was calculated for both complexes and found as 5.6×10^9 and $2.0 \times 10^9 \text{ s}^{-1}$ for *t*-butyl-ZnPc^{•+}:Py-SC₃N@I_hC₈₀^{•-} and ZnPc(SO₂)₈^{•-}:Py-SC₃N@I_hC₈₀^{•+}, respectively.

2.9 Semiconducting single wall carbon nanotube based donor-acceptor systems

Carbon nanotube (CNT) based supramolecular donor-acceptor systems reveal efficient charge separation when hybridized with various photosensitizers linked either by covalent or noncovalent methods [25-34]. CNT based hybrids can be used as primary building block for the design and study of nanomaterial based device engineering for material, electronic, and

catalytic applications. By taking advantage of the huge π network of CNTs, π electron rich organic molecules such as pyrene have been used in noncovalent functionalization through π - π stacking. Additionally, to build supramolecular donor-acceptor hybrids, pyrene was first functionalized with ligands such as imidazole/pyridine capable of metal-ligand axial coordination, ammonium cation for anion-crown ether interaction, and anions/cations for their counter ion interactions [38].

Because of the unique geometry and extended π electronic structure of CNTs, they have become potential candidates to develop light energy harvesting and photovoltaic materials. Two types of semiconducting nanotubes, i.e. (6,5) and (7,6), were noncovalently functionalized with a pyrene-imidazole (Pyr-Im) where the pyrene group was stacked over the CNTs via π - π stacking, leaving behind the imidazole group. The imidazole groups were subsequently used to coordinate ZnP and ZnPc via the metal-ligand axial coordination as shown in Fig. 50 [135]. In this study, the nanohybrid of SWCNTs(*n,m*) with Pyr-Im was prepared by stirring SWCNTs and Pyr-Im at ambient temperature for 48 hours in DMF as a solvent. Later, the mixture was subjected to continuous sonication and centrifugation until the supernatant layer of the solution was clear from Pyr-Im, which was confirmed by UV/Visible and emission spectroscopy. This nanohybrid was later used

Fig. 50. SWCNTs (n,m) based supramolecular donor-acceptor systems to investigate light induced electron transfer process. (a) SWCNT(n,m):Pyr-Im:ZnP (b) SWCNT(n,m):Pyr-Im:ZnPc. (adapted from Ref. 135).

to axially coordinate with ZnP and ZnPc to build a supramolecular donor-acceptor systems to study photoinduced electron transfer processes.

The absorption spectrum of Pyr-Im/SWCNT(6,5) revealed peaks at 583 and 1020 nm while Pyr-Im/SWCNT(7,6) revealed peaks at 664 and 1180 nm. The pyrene absorption bands in the 300-350 nm range were blue-shifted by $2000\text{-}3000\text{ cm}^{-1}$ in the hybrid when compared with pristine Pyr-Im due to π -stacking interactions. The supramolecular assembly involving SWCNTs(n,m) and both ZnP and ZnPc was established using optical absorption spectral methods in DCB. Absorption titration of both nanohybrids Pyr-Im/SWCNT(6,5) and Pyr-Im/SWCNT(7,6) with ZnP and ZnPc revealed the diminishing of Soret band of ZnP (424 nm), and Q band of ZnPc (680 nm) along with clear isosbestic points. Further, fluorescence titration was carried out to investigate the excited state interactions within the system. This study revealed significant quenching of emission from both photosensitizers, ZnP and ZnPc, after the interaction of nanohybrids via metal-ligand axial coordination. Nanosecond transient absorption studies were supportive of photoinduced electron transfer in these hybrids.

Fig. 51. (a) SWCNT:ZnP(alkyl)₄, (b) SWCNT-(alkyl)₄ZnP nanohybrid axially coordinated to C₆₀Im to investigate light induced electron transfer processes. (adapted from Ref. 136).

To further investigate the photoinduced energy/electron transfer processes, a three layer supramolecular assembly possessing fullerene–ZnP–SWCNT was constructed via π -stacking and metal-ligand axial coordination. First, the semiconducting SWCNTs, i.e. (6,5) or (7,6), and ZnP possessing four long alkyl chains were treated for exfoliation and solubilization of the hybrids in organic solvents. Next, C₆₀Im was coordinated with the ZnP/SWCNT hybrid, as shown in Fig. 51 [136].

The preparation of a nanohybrid possessing ZnP and (6,5) or (7,6) SWCNTs was achieved by stirring both components in DMF as a solvent for 48 h at room temperature. The process of sonication and centrifugation was applied to get the pure hybrid by removing unreacted ZnP species from the supernatant which was confirmed by absorption and fluorescence spectral monitoring. The hybrids were characterized by various spectroscopic techniques including HR-TEM imaging. Absorption spectra of the hybrids recorded in DCB revealed the characteristic bands of both species. A band at 424 nm corresponding to ZnP Soret band while the near-IR bands at 1100 or 1180 nm corresponding, respectively, to (6,5) or (7,6) SWCNTs were observed. Upon forming the hybrid ZnP-SWCNTs, a 3 nm blue-shift of the ZnP Soret band along with some broadening, and a 3-4 nm red-shift of the SWCNTs near-IR bands was observed. Addition of C₆₀Im over the ZnP/SWCNTs hybrid revealed additional spectral changes of the hybrid as a result of the metal-ligand axial coordination, which further supported the formation of the three layered supramolecular assembly. The geometry of the three layer hybrids was achieved by performing energy minimization calculations using B3LYP/3-21G(*) method. The three layered hybrid clearly showed the holding of SWCNTs by the alkyl chains from ZnP and the N-atom from the C₆₀Im group axially coordinating to the central Zn atom. The frontier HOMO was located over the ZnP entity while the HOMO-1 was located over the SWCNT. The LUMO was delocalized over both the SWCNT and ZnP whereas the LUMO+1 was predominantly located over the C₆₀ entity.

The fluorescence study of ZnP/SWCNTs revealed approximately 70% quenching of ZnP fluorescence as a result of formation of the double layer nanohybrid. Further quenching of the fluorescence was observed after the addition of C₆₀Im which further confirmed the interaction of C₆₀Im to the ZnP entity of the nanohybrid via metal-ligand axial coordination. Time-resolved

fluorescence and nanosecond transient studies were supportive of occurrence photoinduced electron transfer in these nanohybrids.

3. Conclusions

From the examples discussed here, it is clear that the metal-ligand axial coordination motif seems to be a simple and an elegant approach to building self-assembled supramolecular donor-acceptor systems. Using this approach, model systems capable of performing relatively simple energy and electron transfer processes to rather complex multi-step charge separation processes leading to long-lived charge-separated states have been accomplished. In a majority of these studies, metalloporphyrins and metallophthalocyanines having the central metal ion coordinatively unsaturated have been employed as photoactive sensitizers. On the other hand, C₆₀, possessing favorable redox and low reorganization energy requirement in electron transfer reactions, has been the primary choice as an electron acceptor. Sensitizers such as triphenylamine, BODIPY and SubPc have been used as energy harvesting molecules in the supramolecular constructs. In the majority of these systems, the energy and electron transfer processes initiate from the singlet excited state of the sensitizers. Various spectroscopic techniques have been used to investigate the donor-acceptor conjugate formation, and to probe photoinduced energy/electron transfer processes that occur within these supramolecular conjugates, and also to unravel their mechanistic details. Apart from C₆₀, near-IR absorbing and emitting azaBODIPY seem to serve the role of an energy and/or electron acceptor. Among the other forms of nanocarbons, endohedral fullerene and semiconducting single wall carbon nanotubes are promising for building energy harvesting supramolecular assemblies. Much could be anticipated in the coming years from this intriguing area of research.

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Table of Content

Design and photochemical study of supramolecular donor-acceptor systems assembled via metal-ligand axial coordination

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