



Review Paper

Application of Super-molecules in Solar Energy Conversion- A Review

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Abstract

As molecules are made up by atoms, super-molecules are made up by suitably arranged molecular components. The review concentrates on the recent progress in studies of modified super-molecules and their applications towards solar energy conversion are described. The comprehensive review contains 61 references.

Keywords: Super-molecules, solar energy, photovoltaic cell, calixarene, porphyrin, Fullerene.

Introduction

As the first rays of the Sun creep over the horizon, billions of nature's tiny power plants kick into action. In these small molecules, photons of light from the Sun begin to power the chemical reactions which are essential to life.

Almost everything on Earth ultimately depends on the Sun for the energy to keep going. Photosynthesis allows green plants to grow by transforming carbon dioxide and water from the atmosphere into organic compounds, producing the biomass that sustains almost all animal life on the planet. But while nature pulls energy directly from sunlight, humans go about things the hard way, digging up coal and drilling for oil and gas-obtaining the energy second-hand.

The rapid consumption of fossil fuels has created unacceptable environmental problems such as greenhouse effects, which may lead to disastrous climatic consequences. Thus, renewable and clean energy such as that obtained by using solar cells is required to maintain the quality of human life as well as the environment.

Big is Beautiful: Self-assembling is a basic facet of the physical world: electrons, neutrons and other sub atomic particles assemble into atoms; atoms assemble to give molecules; molecules react with one another to reassemble into new molecules which may contain hundreds and thousands of molecules called macromolecules. When macromolecules interact with one another by certain non-covalent or non-conventional interaction such as dipole-dipole, ion-dipole, ion pairing (electrostatic), hydrophobic and hydrophilic interactions, hydrogen bonding, Van der

Walls interactions etc.; they are termed as super-molecules/supramolecules¹⁻⁴.

A supramolecular assembly possesses amazing structural flexibility and illustrates the binding or a complexation event that takes place between a host and a guest. Host can be a large molecule or aggregate having a sizeable cavity with convergent binding sites; while a guest could be a cation, anion or a neutral molecular species with divergent binding sites. Host-guest chemistry being the cornerstone of supramolecular chemistry has evoked interests from physicists, environmentalists and microbiologists to biotechnologists and it has also fuelled a growing eagerness in the area to such an extent that it is now a well-recognized field in scientific disciplines⁴. Supramolecular chemistry is one of the most vigorous and fast growing fields in chemistry. It has been stated, "Just as there is a field of molecular chemistry based on the covalent bond, there is a field Supramolecular chemistry, the chemistry of molecular assemblies and intermolecular bonds". Supramolecular chemistry is also expressed as the chemistry beyond the molecule or as the chemistry of the non-covalent interactions. J. M. Lehn, D. J. Cram and C. J. Pedersen were awarded Nobel Prize in chemistry in 1987 for pioneering work in the field of supramolecular chemistry¹⁻³. Supramolecules can be classified by their generation on the time scale. Cyclodextrins⁵ and crown-ethers⁶ are the first and second generation supramolecules respectively. Calixarenes are a class of cyclo-oligomers formed by condensation between phenol and aldehyde and are classified as third generation super-molecules/supramolecules, figure 1.

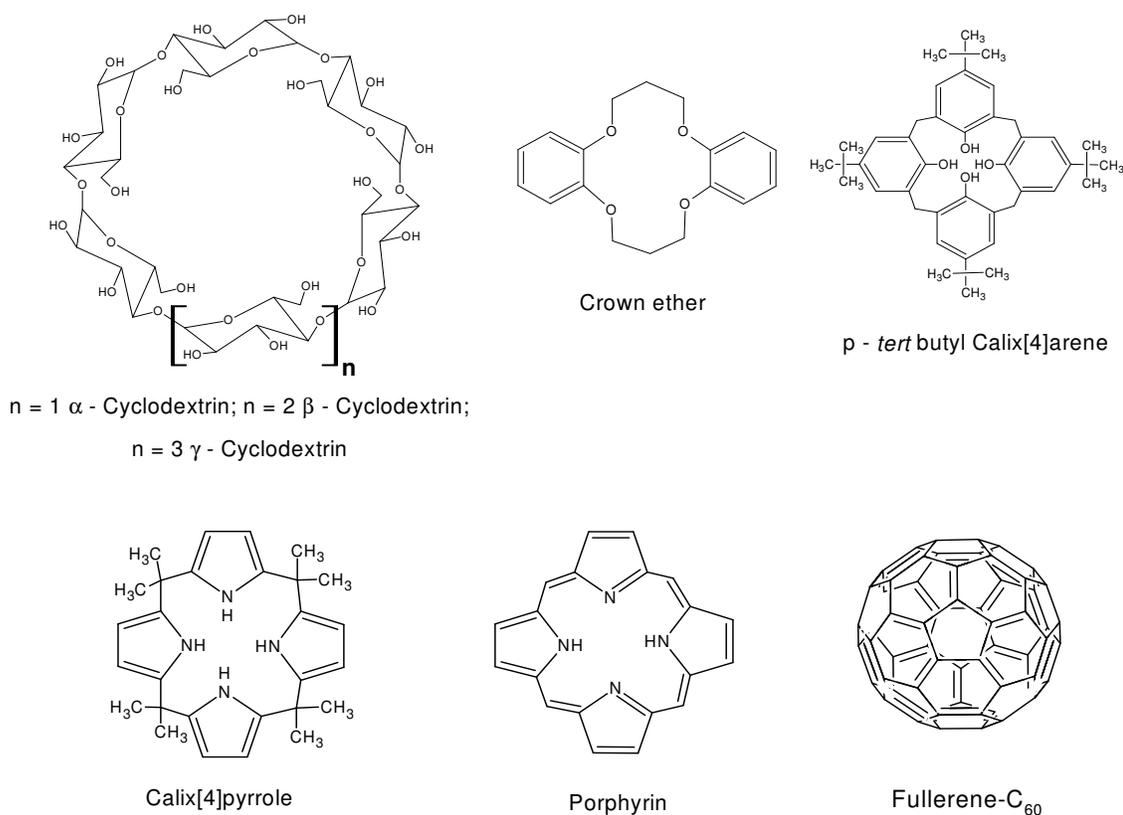


Figure-1
Super-molecules/Supramolecules

The control provided by recognition processes allows the development of *functional molecular* and *supramolecular devices*, defined as structurally organized and functionally integrated systems built from suitably designed molecular components performing a given action (*e.g.* photoactive, electroactive, ionoactive, *etc.*) and endowed with the structural features required for assembly into an organized supramolecular architecture. The chemicals to carry out these diverse tasks, known as supramolecules, are big. Supramolecules are made from several distinct units, each with a particular job to do. For example, one unit might absorb photons of light, another transfer the photons energy, and a third carry out chemical reactions. Because these units can be built separately before being chemically "clipped" together, supramolecules are incredibly versatile. Research scientists can mix and match the units to create supramolecules that are tailor-made for particular tasks.

One thing that all these supramolecules have in common is a light-absorbing unit, essential for receiving photons and soaking up their energy. Some supramolecules do this by "photo-initiated charge separation". The light-absorbing unit captures a photon, and the energy is used to shift an electron from one part of the supramolecule (an electron donor) to

another (an electron acceptor). This gives the donor a positive charge and the acceptor a negative charge, and these are stabilized and held apart. The molecule becomes a tiny battery. This preserves some of the photon's energy as electrical energy. "Designing supramolecular systems based on this idea will work as molecular devices for solar energy conversion using sunlight".

Photovoltaic Cell: Photovoltaic is the direct conversion of light into electricity at the atomic level. Some materials exhibit a property known as the photoelectric effect that causes them to absorb photons of light and release electrons. When these free electrons are captured, electric current results that can be used as electricity. A photovoltaic cell (PV cell) is a specialized semiconductor diode that converts visible light into direct current (DC). Some PV cells can also convert infrared (IR) or ultraviolet (UV) radiation into DC electricity. Photovoltaic cells are an integral part of solar-electric energy systems, which are becoming increasingly important as alternative sources of power utility.

The photoelectric effect was first noted by a French physicist, Edmund Bequerel, who found that certain materials would produce small amounts of electric current when exposed to light. Albert Einstein described the nature

of light and the photoelectric effect on which photovoltaic technology is based, for which he later won a Nobel Prize in physics. The first photovoltaic module was built by Bell Laboratories; it was billed as a solar battery and was mostly just a curiosity as it was too expensive to gain widespread use. In the 1960s, the space industry began to make the first serious use of the technology to provide power aboard spacecraft. Through the space programs, the technology advanced, its reliability was established, and the cost began to decline. During the energy crisis in the 1970s, photovoltaic technology gained recognition as a source of power for non-space applications.

How do photovoltaic work? Figure-2 illustrates the operation of a basic photovoltaic cell, also called a solar cell. The first PV cells were made of silicon combined, or doped, with other elements to affect the behavior of electrons or holes (electron absences within atoms). Other materials, such as copper indium diselenide (CIS), cadmium telluride (CdTe), and gallium arsenide (GaAs), have been developed for use in PV cells. There are two basic types of semiconductor material, called positive (or P type) and negative (or N type). In a PV cell, flat pieces of these materials are placed together, and the physical boundary between them is called the P-N junction. The device is constructed in such a way that the junction can be exposed to visible light, IR, or UV. When such radiation strikes the P-N junction, a voltage difference is produced between the P type and N type materials (light energy strikes the solar cell; electrons are knocked loose from the atoms in the semiconductors materials). Electrodes connected to the semiconductor layers allow current to be drawn from the device—that is, electricity.

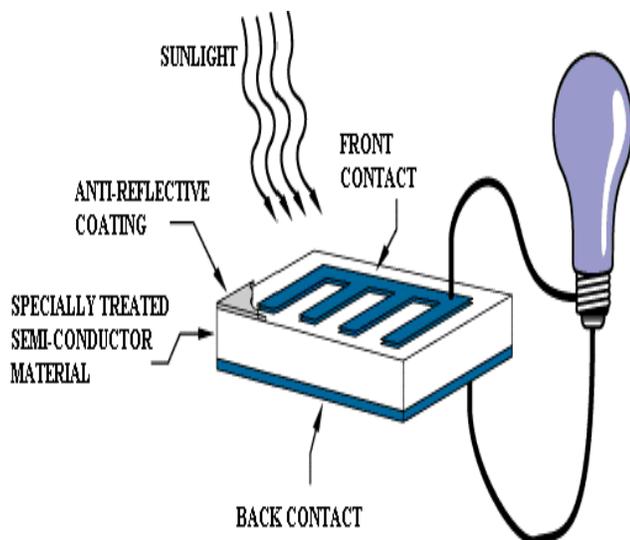


Figure-2
Representation diagram of photovoltaic system

This electricity can then be used to power a load, such as a light or a tool.

A number of solar cells electrically connected to each other and mounted in a support structure or frame is called a photovoltaic module. Modules are designed to supply electricity at a certain voltage, such as a common 12 volts system. The current produced is directly dependent on how much light strikes the module. Multiple modules can be wired together to form an array. In general, the larger the area of a module or array, the more electricity will be produced. Photovoltaic modules and arrays produce direct-current (dc) electricity. They can be connected in both series and parallel electrical arrangements to produce any required voltage and current combination. The use of PV cells and batteries for the generation of usable electrical energy is known as photovoltaic. Over the past 15 years, supramolecules have received much attention due to their unique chemical and physical properties as well as their potential applications^{4, 7, 8} in coatings, additives, drug and gene delivery, macromolecular building blocks, nanotechnology, and supramolecular science. Because a number of comprehensive reviews have been published on supramolecules, research involving solar energy conversation is emphasized here. In addition, increasing energy consumption and rising energy prices in the world forces to look for energy alternatives, one of the most promising is being the photovoltaic solar energy conversion. So, in this comprehensive review article, various concepts and device architectures of organic solar cells which are derived from super-molecules are described.

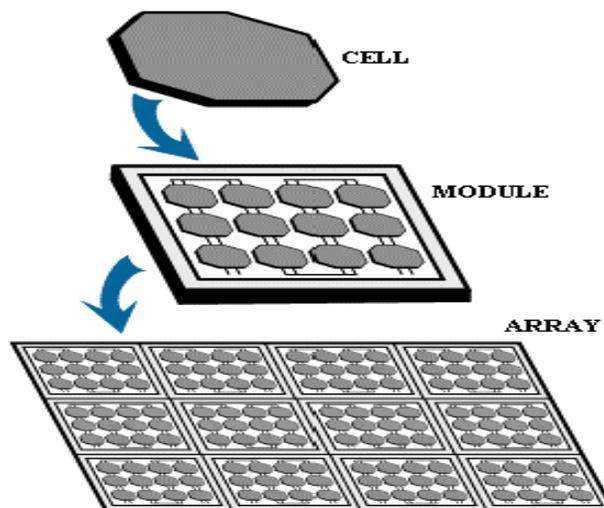


Figure - 3
Cell, Module and array

Review of Research and Development in the Subject

Supramolecular photochemistry as well as solar cells is fascinating topics of current interest in inorganic photochemistry and very active research fields which have attracted wide attention in last two decades. Three types of supramolecular systems have been the focus of this work: (i) cage-type coordination compounds; (ii) second-sphere coordination compounds, exemplified by ion-pair photochemistry of cobalt complexes and (iii) covalently-linked systems.

Solar energy conversion and development of thin-layer photo-electrochemical solar cells based on sensitization of nano-crystalline semiconductor films by some ruthenium polypyridyl complexes are presented as an important application that resulted from specifically engineered artificial assemblies⁹. As is well-known, polymer photovoltaics promise flexibility and high efficiency through excellent absorption cross-sections for use in solar cells^{10,12}. However, they suffer from a severe mismatch in length scale, strong fluorescence, and morphological control.

Formation of a controlled fullerene mesophase within an organic host system has enabled us to create high-power conversion efficiency photovoltaics¹³. The best known nanomaterial to create such "bulk hetero-junctions" is the fullerene and its derivatives. Since the hole is typically the high mobility carrier, in the regio-regular poly(3-hexylthiophene) (P3HT) case,¹⁴ enhancing electron mobility further serves to provide charge balance to devices. While this has worked well, the hopping nature of electrons in sub-percolating networks of fullerenes severely limits the maximum obtainable efficiency. What is needed is control over the structure of the nano-phase that will allow for tailored carrier mobilities. To control the mesophase, we have attempted to create single crystalline nano-whiskers of 1-(3-methoxy carbonyl)propyl-1-phenyl-(6,6)C61 (PCBM) pointing toward the cathode (but not touching it) from the anode. This provides an increase in the electron mobility more closely matching that of the holes in the P3HT. We demonstrate this mesophase control in the P3HT: PCBM system, famed for its possible applications to organically based solar cells¹⁵⁻¹⁸.

Organic composites or organic/inorganic mixed nanocomposites promise to be valuable in solar energy conversion, photovoltaics, and catalytic reactivity, specifically in novel chemical and light driven systems¹⁹. Thus, their production has visibly increased their potential impact on a broad range of innovative technologies. The extraordinary charge transfer properties of fullerenes, especially the small reorganization energy that fullerenes exhibit in electron transfer reactions, has resulted in remarkable advances in areas of light-induced charge separation and solar-energy conversion²⁰. However, mixed nano-composite materials – with fullerenes as a key electron

acceptor component -of well-defined composition and stoichiometry have hardly ever been tested²¹. One of the major setbacks is the insufficient solubility of nanocomposites that carry more than a single C₆₀ component and the lack of control over their production.

Why fullerene so promising for photovoltaics? We consider the following causes that make C60 unique among all known semiconductors, and in particular, promising for photovoltaic applications. There is probably no more environmentally benign semiconductor than C60 in that it can be synthesized from graphite using nothing more than a beam of concentrated solar energy, and subsequently purified and crystallized using the same energy source. Early studies²¹ of C60 as a material for inorganic solar cells was instigated by the theoretical prediction that a C60 crystal has a direct band gap of 1.5 eV. On one hand, this value is close to the experimental value of about 1.6 eV for the fundamental edge in the optical absorption spectra and that of 1.7 eV for the photoconductivity spectra of C60 thin films. On the other hand, this is the optimal value for high efficiency photovoltaic devices of the single junction type. For organic donor-acceptor solar cells, a C60 molecule is an ideal candidate for acceptor because of its high electron affinity (2.65 eV). Such cells are now becoming a serious alternative to conventional inorganic photovoltaic devices due to a number of potential advantages, such as their lightweight, flexibility and low cost fabrication of large areas. The efficient photo response of the donor-acceptor cells consisting of conjugated polymers and fullerenes²¹.

The layer-by-layer (LBL) technique, which emerged as a powerful technique for the modification of photoactive electrodes and preparation of unique nanostructured films, can be a convenient tool for utilizing electrostatic attraction and electron delocalization in optoelectronic devices²². Electrostatic and van der Waals binding of water-soluble C₆₀ derivatives (C₆₀). To CdTe nanoparticles (NPs) creates a functional interface, which, subsequently facilitates rapid electron transfer. The versatility of NP chemistry and the LBL deposition process opens up exciting possibilities for further engineering of the redox processes on the electrodes²³.

On the other hand, modification of wide band gap semiconductor surfaces by a new generation of supramolecular sensitizers combining porphyrin and ruthenium-polypyridyl complexes leads to versatile molecular interfaces, allowing the exploitation of photo-induced charge transfer in photo-electrochemical devices. All the chromophore groups, porphyrin and peripheral ruthenium complexes are contributing to the photocurrent²⁴. In the case of porphyrin systems, there is an agreement that electron injection occurs from the lowest singlet excited state. For the tetra-ruthenated porphyrins, the mechanisms involved in electron transfer are more complex, since both components

are responsible for photocurrent generation. As already discussed, from the HOMO and LUMO compositions, the peripheral ruthenium complexes can effectively transfer electronic charge to the porphyrin center via Ru (II) porphyrin MLCT transitions. Finally, we have also shown that the direct interaction between the ZnTPyP core and TiO₂ plays an important role in the photoresponse efficiency. Because of the several aspects involved, efforts are being directed in various research-laboratories to improve the photon energy conversion, particularly, to find a better commitment between solubility and aggregation of the different modifiers.

Bignozzi et al. were the first ones to exploit the photoinduced charge separation and antenna properties of supramolecular polypyridyl metal complexes²⁵. Porphyrins, phthalocyanines, and related macrocycles such as *meso*-tetrapyrrolylporphyrins and *meso*-tetraphenylporphyrins have been extensively employed as building blocks for assembling supramolecular systems, stimulated by their photochemical, electrochemical, and catalytic properties²⁶⁻²⁸. These organic dyes are also well-known TiO₂ sensitizers due to their strong absorption at 400-450 nm (B or Soret band) and 500-700 nm (Q bands).

The development of more complex systems, especially within the framework of supramolecular chemistry, gives rise to the possibility of designing organized systems as components of molecular level photochemical devices.²⁹ Supramolecular systems are constituted of a number of discrete molecular components with definite individual properties, held together by chemical interactions. This organization is particularly interesting for the development of systems capable of performing useful functions, such as use of light for energy or information purposes³⁰.

Molecular devices are assemblies of molecular components designed to achieve specific functions, such as photoinduced electron and energy transfer in solar energy conversion, electron collection, remote photo-sensitization, antenna effect, photo-switching of electric signals, light-energy up conversion, photoinduced structural changes in switch on/off applications (photo-isomerizable systems), molecular wires and sensors, in analytical chemistry, and in the development of new materials and nano-scale electronic devices³¹.

Also, regenerative photo-electrochemical cells and some ruthenium complexes used as sensitizer for charge injection into nano-crystalline semiconductors will be presented to illustrate an application that has evolved from a fundamental investigation of inorganic photochemistry by use of a specifically designed assembly to conceive artificial molecular devices. Chemically-based systems such as photovoltaic and photo-electrochemical cells have been developed as an alternative to solid-state silicon-based cells for the conversion of solar energy into electricity³². The use of coordination compounds as light absorbers, for instance

[Ru(bpy)₃]₂⁺ was one of the first approaches to convert low-energy starting materials into high-energy products, such as H₂O into H₂ and O₂, in homogeneous cells.

The use of photo stable wide band-gap semiconductors would require high-energy light to create electron hole pairs and dye sensitization was of limited utility because of sub-monolayer coverage and low absorptivities, although it presented advantages over direct band to band excitation as in conventional solar cells due to the reduction of electron-hole recombination. The development of mesoporous membrane type film with large surface areas prepared from nano sized colloidal semiconductor dispersion caused a remarkable growth in the field³³. Dye sensitization of nano-structured wide band-gap semiconductors has led to an extension of their photo response into the visible region and to efficient conversion of solar energy into electricity in photo-electrochemical devices³⁴. Similarly to chlorophyll molecules, adsorbed dyes act as light absorbing antenna to mimic the photosynthetic process by promoting photo induced charge separation in an organized molecular structure on the nanometric scale. In this approach, attached dyes, rather than the semiconductor itself, are the absorbing species and upon excitation inject electrons into the semiconductor conduction band which are then collected at a conducting surface, keeping the electron-hole pair separated and generating photocurrent. As a result of this advance, the development of low-cost efficient photochemical solar cells became possible³⁵.

Photovoltaic cells and fluorescence sensing are two important areas of research in chemistry. The need for clean and renewable energy sources has increased interest in solar power. Photovoltaic cells based on organic components provide the possibility of inexpensive devices. In both photovoltaic and fluorescence sensing systems, a photon of light is absorbed, which creates an excited state in the system. Energy, sometimes in the form of an electron, is then transferred from the excited donor group to an acceptor group of lower energy. In the case of solar cells, an electron must be channeled to perform work.

In molecular-based photovoltaic devices, one of the most established examples is dye-sensitized solar cells (DSSC). In these systems, a monolayer of the light absorbers (dye molecules) self-assembles on high surface area electrodes based on nano-crystalline, mesoporous metal oxide such as TiO₂ and the energy is transferred from the dye to the metallic system. Two of the major concerns in developing dye-sensitizer molecular systems are: broad spectral overlap with solar irradiation and efficient electron-transfer within the system. One of the strategies employed to improve the function of supramolecular dye system is the addition of secondary donor/acceptor species. A transition metal center linked to an organic chromophore such as porphyrin will also

largely add to the number of electron or energy transfer reactions within the assembly.

These novel classes of supramolecules incorporating both porphyrin and Ru(II)-trisbipyridine species as dye sensitizer for photonic devices. Supramolecules based molecular devices will be synthesized by pyrrole and various substituted aromatic aldehydes in presence of acid. Some of their proposed structures are presented in figure 4.

Many fullerene-based supramolecules have been proposed as potential organic photovoltaic devices, with their electrochemical and photo-electrochemical properties measured under light illumination. Phthalocyanine possesses good electron-donating properties due to its large easily ionised π -electron system, whereas fullerene is good π -electron acceptor which can be connected with other organic molecules. A phthalocyanine – fullerene – based supramolecular system³⁶ is therefore a potential material candidate for a photovoltaic cell due to its large and flexible absorption combined with electrical properties similar to an inorganic semiconductor. Hiroshi M et al. investigated the geometric and electronic structure of phthalocyanine–fullerene supramolecule using an initio quantum mechanical calculation. The results suggest that the lowest unoccupied molecular orbital (LUMO) state of this supramolecule

localized on the fullerene and the highest occupied molecular orbital (HOMO) state is localized on half of the phthalocyanine. The energy difference of localized LUMO levels strongly depended on the functional group attached to the phthalocyanine and the structure of the supramolecule.

Leising G. et al. have been investigated the morphological aspects of blend layers prepared from a blue-green light-emitting conjugated polymer (methyl-substituted ladder-type poly(*p*-phenylene), mLPPP), blended with either a crown ether, Dicyclohexano18crown6 (DCH18C6) or a high-molecular-weight poly(ethylene oxide) (HMWPEO), and a Li salt, lithium trifluoromethanesulfonate (LiCF₃SO₃, Litriflate, LiTf for short) as a solid state electrolyte as they were successfully applied as active layers in light-emitting electrochemical cells (LECs)³⁷. The surface morphologies of the blends were investigated by atomic force microscopy (AFM) in Tapping mode© and the ion distribution with X-ray analysis by energy-dispersive X-ray spectrometry (EDXS) in the scanning electron microscope (SEM). The specific phase morphologies of the blends, the complexation of the ions and the ionic transport numbers were found to have tremendous influence on the performances of the corresponding LECs revealing either rectifying or symmetric optoelectronic characteristics in forward and reverse bias directions.

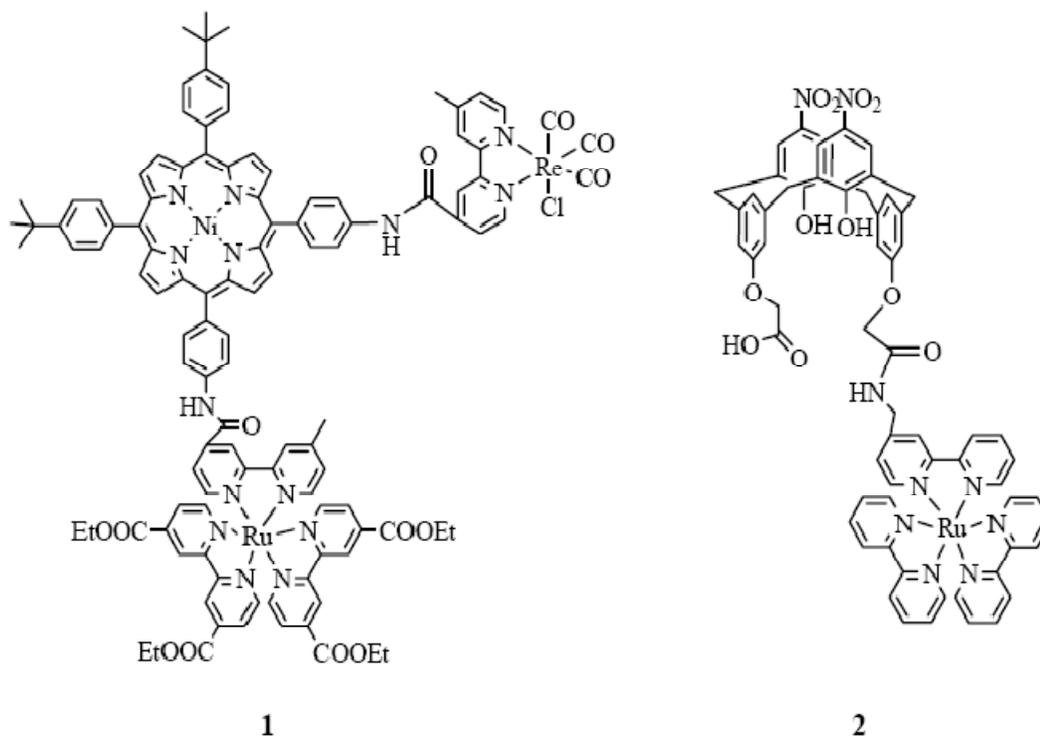


Figure-4
Novel classes of supramolecules as dye sensitizer for photonic devices

Review articles deal with the progress in studies of polymeric covalent and noncovalent modifications of fullerenes (mainly C_{60}) and carbon nanotubes (CNTs), and their applications³⁸. By using functional polymers to react with fullerenes, or synthesizing polymers in the presence of fullerenes, various kinds of polymeric fullerenes can be prepared: side-chain polymers, main-chain polymers, dendritic fullerenes, star-shaped polymers, fullerene end-capped polymers, etc. Furthermore, by controlling the functional groups in polymer chains and reaction conditions, many well-defined fullerene polymers have been prepared. 'Living' polymerization methods have also been introduced for preparation of fullerene polymers, e.g. anionic polymerization, stable free radical polymerization, and atom-transfer free-radical polymerisation. With these living methods, both the architecture of the fullerene polymers and the grafted polymer chains can be well-controlled. All of these methods establish a good platform for developing applications of fullerene polymers. The synthesis of polymeric CNTs is only in its infancy. However, present results show promise that the combination of the unique properties of CNTs with functional polymers will lead to novel materials with unusual mechanical, electrical, magnetic, and optical properties. Doping of polymeric systems with fullerenes is also a very important research area, especially for preparation of electronic and optical materials. Both conducting and conventional polymers can be used as matrices in the preparation of functional composites. The structures and properties of these composites are strongly dependent on the properties and concentrations of the active components. CNT-doped polymers have also been prepared and show interesting properties. The combination of the unique properties of fullerenes and CNTs with polymers makes these materials potential candidates for many applications, such as data storage media, photovoltaic cells and photodiodes, optical limiting devices, photosensitive drums for printers, and so on.

Fullerene (C_{60}) / poly (methylphenylsilane) (PMPS) photovoltaic cells were fabricated with various concentrations of C_{60} and their photovoltaic properties were investigated.³⁹ The characteristic PL peak of PMPS was significantly quenched in C_{60} /PMPS and the photocurrent of a C_{60} /PMPS device was much higher than that of a PMPS single layer device. This indicates that the addition of C_{60} to PMPS enhanced the separation efficiency of electron-hole pairs. It was found that the performance of a PMPS device was dramatically improved by blending C_{60} .

Organic photovoltaic cells made using supramolecular complexes of porphyrin dendrimers with fullerenes demonstrate remarkable enhancement in the photo electrochemical performance as well as broader photo response in the visible and near-infrared regions relative to the reference system reported.⁴⁰ This demonstrates that

molecular assemblies of C_{60} and porphyrins with dendritic structures are effective in photo-energy conversion systems.

Chengwu S. et al. have studied the influence of different cations on redox behavior of I^- and I_3^- by cyclic voltammetry and electrochemical impedance spectroscopy⁴¹. It was demonstrated that increasing cation size tends to give rise to higher reductive activity of I^- and lower diffusion coefficient of I_3^- in these cations, alkylimidazolium, $[Na \subset 15-C-5]^+$ and $[K \subset 18-C-6]^+$. Moreover, they have mentioned that the performance of dye-sensitized solar cells (DSCs) with electrolyte containing $[K \subset 18-C-6]I$ or 1,2-dimethyl-3-propylimidazolium iodide (DMPII). It was found that dye-sensitized solar cells (DSCs) with $[K \subset 18-C-6]I$ give a little higher short-circuit photocurrent density and a little lower fill factor than DSCs with DMPII.

Jean-François N. et al. have reported the synthesis and the study of fullerene-containing supramolecular photoactive devices⁴². Their research approach is based on the self-assembly of C_{60} derivatives bearing an ammonium unit with functionalized crown ethers. The ammonium-crown ether interaction itself is weak and the K_a values are rather low when the association results only from the binding of the cationic unit with the macrocyclic component. However, when additional recognition elements are present, the stability of the complexes can be dramatically increased. This principle is illustrated with various examples of systems resulting from the self-assembly of C_{60} -ammonium derivatives and crown ethers bearing a porphyrin or an oligophenylenevinylene chromophore.

Photovoltaic devices built by a hierarchical self-assembly process using hydrogen-bonding terminated self-assembled mono layers (SAMs) on gold and the combination of a hydrogen-bonding barbituric acid appended fullerene and a complementary melamine terminated π -conjugated thiophene-based oligomer are reported⁴³. The incorporation of these electron donor (oligomer) and electron acceptor (methanofullerene) assemblies into simple photovoltaic (PV) devices as thin films leads to a 2.5 fold-enhancement in photocurrent compared to analogous systems comprising non-hydrogen-bonding C_{60} -oligomer systems, which is ascribed to higher molecular-level ordering. The modification of the gold electrode surface with self-assembled mono layers bearing hydrogen-bonding molecular recognition end groups was seen to further enhance the PV response of the corresponding functional supramolecular device. This superposition of two types of self-assembly facilitates the generation of binary supramolecular fullerene-containing architectures.

A variety of molecular assemblies of porphyrin as a donor and fullerene as an acceptor on electrodes for molecular photoelectrochemical devices have constructed⁴⁴. Highly efficient energy- and electron-transfer processes have been

realized at gold electrodes modified with self-assembled monolayers of porphyrin- or fullerene linked systems mimicking light-harvesting and charge separation in bacterial photosynthesis. Highly ordered organization of porphyrins and fullerenes has also been achieved using step-by-step self-assembly of porphyrin and fullerene units by association with gold nanoparticles or dendrimers on tin oxide electrodes, which exhibit high power-conversion efficiency of up to 1.5%. These results will provide valuable information on the design of donor-acceptor type molecular assemblies that can be tailored to construct highly efficient organic solar cells.

A versatile method for film fabrication of fullerene/porphyrin mixed composite films has been reported⁴⁵. Thin films consisting of two fullerene-pyrrolidine derivatives and a water-soluble porphyrin, TPPS4, were prepared by the Langmuir-Schäfer (LS, horizontal lifting) method. In particular, a solution of the fullerene-pyrrolidine in chloroform and dimethyl sulfoxide was spread on the water surface, while the porphyrin (bearing peripheral anionic sulfonic groups) was dissolved into the aqueous sub phase. Evidence of the effective interactions between the two components at the air-water interface was obtained from the analysis of the floating layers by means of surface pressure vs area per molecule Langmuir curves, Brewster angle microscopy and UV-visible reflection spectroscopy. The characterization of the LS films by UV-visible spectroscopy reveals that in each case the two constituents behave as strongly interacting pi systems. The use of polarized light suggests the existence of a preferential direction of the TPPS4 macrocyclic rings with an edge-on arrangement with respect to the substrate surface, regardless which fullerene-pyrrolidine derivative is in the composite film. Atomic force microscopy investigations give evidence of morphologically flat layers even for LS transfer at low surface pressures. Photo-action spectra were recorded from films deposited by only one horizontal lifting onto indium-tin-oxide (ITO) electrodes, and the observed photocurrent increased notably with increasing transfer surface pressure for both derivatives composite films.

Semi-empirical and density functional molecular orbital calculations are performed on fullerene derivatives with varying reduction potentials, successfully used as an electron acceptor in bulk hetero-junction solar cells⁴⁶. The geometries of all the compounds were optimized with the semi-empirical PM3 method. Density functional theory (DFT) single-point calculations, B3LYP/3-21G*, have been carried out with the aim to investigate the energy levels of the frontier orbitals. Authors have correlated the theoretical lowest unoccupied molecular orbital (LUMO) levels of different fullerenes with the open-circuit voltage of the photovoltaic device based on the blend of poly[2-methoxy-5-(3,7-dimethyloctyloxy)]-1,4-phenylenevinylene (MDMO-PPV) with the acceptor molecules. Author have also investigated the influence of new substituents on the LUMO level of the parent fullerene

showing the possibility to further increase the open-circuit voltage of the MDMO-PPV: fullerene device.

On the other hand, Photo-catalytic generation of hydrogen from water is an integral part of the next generation clean fuel technologies. The conversion of solar energy into useful chemical energy is of great interest in contemporary investigations. The splitting of water is a multi-electron process involving the breaking and making of chemical bonds which requires multi-component photo-catalytic systems.

Supramolecular complexes $[(TL)_2Ru(BL)_2RhX_2](Y)_5$ (where TL = terminal ligand, BL = bridging ligand, X = Cl⁻ or Br⁻, and Y = PF₆⁻ or Br⁻) have been synthesized and studied for their light absorbing, electrochemical and photo-catalytic properties⁴⁷. The supramolecular complexes in this investigation are multi-component systems comprised of two ruthenium based light absorbers connected through bridging ligands to a central rhodium, which acts as an electron collecting center upon excitation. These complexes absorb light throughout the ultraviolet and visible regions of the solar spectrum. The supramolecular complexes possess ruthenium based highest occupied molecular orbitals (HOMO) and a rhodium based lowest unoccupied molecular orbital (LUMO). These molecular devices have been investigated and shown to function as photo initiated electron collectors at the reactive rhodium metal center, and explored as photo-catalysts to generate hydrogen from water in an aqueous solution in the presence of an electron donor.

Two series of novel *meso*-substituted porphyrins, namely 5,10,15,20-*tetra*[4-(3-phenoxy)propoxy]phenyl porphyrin, the structural analogue 5,10,15,20-*tetra*[2-(3-phenoxy)propoxy]phenyl porphyrin and their Co(II) Cu(II) and Zn(II) complexes were synthesized⁴⁸. The compounds were characterized using various spectroscopic techniques and their molecular structure was proposed based on density functional theory calculations. The diverse properties of the porphyrin derivatives result from the different stereochemistry of the particular substituents at the *meso* site on the macrocycle and are controlled also by the coordinated metal. The ¹H NMR spectrum of the free-base porphyrin showed a complicated spin-splitting. The photo-catalytic activities in degradation of 4-nitrophenol were investigated using polycrystalline TiO₂ impregnated with the porphyrins and metallo-porphyrins. The Cu(II) porphyrin was a more effective sensitizer than other metal containing compounds (M = Co, Zn) as well as the free-base. Photo-catalytic activity was also influenced by spatial positions of the substitutions on the porphyrin molecules.

Moreover, Morvillo P. has used quantum chemical methods to study the energy levels of the frontier orbitals of higher fullerene derivatives (from C₇₀ to C₈₄ and having the same addend as in [6,6]-phenyl C₆₁-butyric acid methyl ester) with the aim to understand if they can be used as electron

acceptors in bulk hetero-junction polymer–fullerene solar cells⁴⁹. Higher fullerenes have a stronger and broader absorption compared to C₆₀ and they can improve the current output of the corresponding devices. The geometries of all the compounds were optimized with the density functional theory at the B3LYP/3-21G* level of calculation. The lowest unoccupied molecular orbital (LUMO) levels of the investigated compounds correlate well with the reduction potentials (obtained by cyclic voltammetry) of the already prepared species. The results indicate that the LUMO level depends not only on the fullerene size (number of carbons of the cage) and constitutional isomer, but also on the position and, in some cases, the addend orientation. This issue should be considered because for a proper device operation, a well-defined LUMO is required. The position of the LUMO level of some higher fullerene derivatives can be suitable for low-band gap polymers.

Barry P.R. et.al. have demonstrated photocurrent enhancement of up to 20% in polymer: fullerene bulk hetero-junction photovoltaic cells *via* the incorporation of a phosphorescent dopant, without degradation in the open-circuit voltage or fill factor of the device⁵⁰. The enhancement is shown to originate from multiple sources. First, the phosphor is able to populate the long-lived triplet state of the polymer, leading to longer diffusion length and a larger polymer contribution. Also, there is direct absorption on the dopant leading to enhanced spectral coverage. Finally, the dopant acts as a donor site and therefore increases the fullerene signal.

The photo-physical and photochemical properties of the tetra- and octa-12-crown-4-substituted zinc (II) phthalocyanines are reported.⁵¹ The new compounds have been characterized by elemental analysis, IR, ¹H and ¹³C NMR spectroscopy, electronic spectroscopy and mass spectra. General trends are described for photo-degradation, singlet oxygen and fluorescence quantum yields, and fluorescence lifetimes of these compounds in dimethylsulphoxide (DMSO). Photo-physical and photochemical properties of phthalocyanine complexes are very useful for photodynamic therapy (PDT) applications. The effects of the substituents on the photo-physical and photochemical parameters of the zinc (II) phthalocyanines derivatives are also reported. The singlet oxygen quantum yields (Φ_{Δ}) ranged from 0.48 to 0.78 are indicating the potential of the complexes as photo-sensitizers in applications of PDT.

Oligomeric supramolecules with double- (2H-P), triple- (3H-P) and quadruple H-bonding sites (4H-P) at their both chain ends of PEG (*M*_w = 2000) are successfully utilized to increase energy conversion efficiency for solid state dye-sensitized solar cells⁵². The improved energy conversion efficiency is due mostly to the deeper penetration of the liquid oligomeric supramolecular electrolytes into the

nanopores of the TiO₂ layer, followed by *in situ* self-polymerization *via* multiple H-bonds and the improved ionic conductivity. Among the three solid state dye-sensitized solar cells, the 2H-P and 3H-P electrolytes shows better photovoltaic performances than the 4H-P electrolyte. The difference in the performance is mostly attributable to the fact that the 2H-P and 3H-P electrolytes have a slower electron recombination rate and a faster ionic diffusion coefficient, compared to the 4H-P electrolyte. Therefore, the characters of the liquid and the solid states of the supramolecules may have been able to be successfully utilized to increase the energy conversion efficiency over 4% for solid state dye-sensitized solar cells.

Moreover, Solid-state dye-sensitized solar cells (DSSCs) have been constructed employing supramolecular electrolytes with multiple hydrogen bonding⁵³. A supramolecule was facilely synthesized by one-pot reaction between the amines of methyl isocytosine (MIC) and the epoxy groups of poly(ethylene glycol diglycidyl ether) (PEGDGE) to produce quadruple hydrogen bonding units. Hydrogen bonding interactions and dissolution behavior of salt in supramolecular electrolytes are also investigated by authors. The ionic conductivity of the supramolecular electrolytes with ionic liquid, i.e. 1-methyl-3-propylimidazolium iodide (MPII) reaches 8.5×10^{-5} S/cm at room temperature, which is higher than that with metal salt (KI). A worm-like morphology is observed in the FE-SEM micrographs of TiO₂ nanoporous layer, due to the connection of TiO₂ nano-particles resulting from adequate coating by electrolytes. DSSCs employing the supramolecular electrolytes with MPII and KI exhibit an energy conversion efficiency of 2.5% and 0.5%, respectively, at 100 mW/cm², indicating the importance of the cation of salt. Solar cell performances were further improved up to 3.7% upon tuning interaction strength in the electrolytes.

The photo-physical investigations on non-covalent interaction of a C₆₀-derivative, namely, *tert*-butyl-(1,2-methanofullerene)-61-carboxylate (1) with H₂- (H₂-Pc) and Zn-phthalocyanine (Zn-Pc) in toluene medium have reported⁵⁴. Well defined charge transfer (CT) absorption bands have been located in the ground state. Utilizing the CT absorption bands, various consequential physico-chemical parameters like oscillator strength, transition dipole moment, resonance energy, electronic coupling element and solvent reorganization energy, have been estimated for the complexes of 1 with phthalocyanines. The influence of 1 on the spectral characteristics of H₂- and Zn-Pc are explained using a theoretical model that takes into account the interaction between electronic subsystems of 1 with the phthalocyanines (Pcs). Steady-state fluorescence experiment reveals large binding constants in the magnitude of 68,775 and 31,750 dm³mol⁻¹, for the 1:1 complexes of 1 with H₂- and Zn-Pc, respectively.

The effects of crown ethers (CEs) on the performance of quasi-solid-state dye-sensitized solar cells (DSSCs) have been investigated⁵⁵. Nano-composite silica was used to form gel matrices in the electrolytes, which contained lithium iodide (LiI) and iodine (I₂) in 3-methoxypropionitrile (MPN) solvent. Three types of CEs, 12-crown-4 (12-C-4), 15-crown-5 (15-C-5), and 18-crown-6 (18-C-6) were used as additives to the gel electrolytes. DSSCs containing CEs showed enhancements in solar-to-electricity conversion efficiencies (η), with reference to the one without them. The crown ether, 15-C-5, with a size of cavity matching with the size of Li⁺ in the electrolyte rendered for its DSSC the best performance with an η of 3.60%, under 100 mW/cm² illumination, as compared to 2.44% for the cell without any CE. Enhancements in the photovoltaic parameters of the cells with the CEs were explained based on the binding abilities of the CEs with lithium ions (Li⁺) in the electrolyte. Linear sweep voltammetry (LSV) measurements and electrochemical impedance spectra were used to substantiate the explanations.

A new system for photo induced hydrogen production has been constructed and using a porphyrin-pyrene conjugate functionalized Pt nano-composite as a photo-catalyst and ethylene di-amine tetra-acetic acid (EDTA) as a sacrificial reductant in the absence of an electron mediator⁵⁶. Detailed spectral, computational and photochemical studies reveal that a photo induced energy transfer from the photo excited state of pyrene to the porphyrin occurs, accompanied by an electron transfer from the excited porphyrin moiety to the platinum catalyst for the H₂ generation. Efficient photo-catalytic hydrogen evolution from the system demonstrates the possibility of constructing a photo-catalytic system that uses a Pt nano-composite functionalized by self-assembled donor-acceptor conjugates as a photo-catalyst. The turnover numbers (TON_{Pt} and TON_{dye}) and quantum yields of hydrogen for the photo induced hydrogen production system are 63, 6311, and 2.65%, respectively, and are calculated on the basis that the total amount of H₂ evolved after 12 h of irradiation.

On the other hand, four new Co(II) coordination complexes, [Co(o-phta)(pz)₂]_n 1, [Co(PTA)₂(Imh)₂](HPTA)·H₂O 2, {[Co(pdc)₂(H₂O)](ppz)·2H₂O]_n 3, [K₂Co₂(ox)(btec)(CH₃OH)₂]_n 4, (H₂phta = o-phthalic acid, pz = pyrazole, HPTA = p-toluic acid, ppz = piperazine, Imh = imidazole, H₂pdc = pyridine-2,5-dicarboxylic acid, H₂(ox) = oxalic acid, H₄btec = 1,2,4,5-benzenetetracarboxylic acid), were hydrothermally synthesized and characterized by X-ray single crystal diffraction, IR, UV-Vis absorption spectrum, TG analysis and elemental analysis⁵⁷. The surface photo-voltage properties of the four Co(II) complexes were investigated by the surface photo-voltage spectroscopy (SPS). The structural analyses indicate that complexes 1 and 3 are 1D coordination polymers and

complex 2 is a mononuclear molecular complex. Complexes 1, 2 and 3 are connected into 2D supramolecules by hydrogen bonds, respectively. Complex 4 is a coordination polymer with 3D structure, exhibiting a 4-nodal (4, 5, 6, 12)-connected topology with a Schläfli symbol of (4¹⁰)₂ (4²⁴.6³².8¹⁰) (4⁵.6)₂ (4⁹.6³.8). The results of SPS shows the four complexes exhibit obvious photovoltaic responses in 300 ~ 800 nm, which indicates they all possess photo-electric conversion properties. By the comparative analysis of the SPS, it is found that structure of the complex, species of ligand and coordination micro-environment of the Co(II) ion affect the SPS. The relationships between SPS and UV-Vis absorption spectra are also discussed by authors⁵⁷.

Two C₆₀ derivatives, biindene-C₆₀ monoadduct (BC₆₀MA) and biindene-C₆₀ bis-adduct (BC₆₀BA), were synthesized by one-pot reaction of 1, 1'-biindene and C₆₀, for the application as acceptor materials in Polymer Solar Cells (PSCs)⁵⁸. The two C₆₀ derivatives possess good solubility in toluene and o-dichlorobenzene, and the solubility of BC₆₀BA is even better than that of BC₆₀MA. The electrochemical properties and the LUMO energy levels of the two fullerene derivatives were investigated by cyclic voltammetry. The LUMO energy levels of BC₆₀MA and BC₆₀BA were 0.06 and 0.17 eV higher (up-shifted) than that of PCBM, respectively. The PSCs based on P3HT as donor and BC₆₀MA or BC₆₀BA as acceptor exhibited higher V_{oc} of 0.68 and 0.82 V, respectively, which is benefited from the higher LUMO energy levels of the C₆₀ derivatives. The power conversion efficiency of the PSC based on P3HT/BC₆₀MA was 2.21% after annealing at 140 °C for 5 min.

The synthesis of novel 6,7-[(12-crown-4)-3-[p-(3,4-dicyanophenoxy)phenyl]coumarin (1), 6,7-[(12-crown-4)-3-[p-(2,3-dicyanophenoxy)phenyl]coumarin (2), and their corresponding tetra-(chromenone 12-crown-4)-substituted zinc (II) phthalocyanine complexes (3 and 4) have been prepared⁵⁹. These new compounds have been characterized by elemental analysis, ¹H NMR (1 and 2), MALDI-TOF, IR and UV-Vis spectral data. The fluorescence intensity changes for 1 and 2 by addition of Na⁺ or K⁺ ions have been determined at 25°C in THF. Intensity of the binding Na⁺- and K⁺-complexes (1 and 2) has decreased. The effects of the chromenone crown ether on the phthalocyanine molecule concerning photo-physical and photochemical properties are also investigated. Photo-degradation, singlet oxygen, fluorescence quantum yields, and fluorescence lifetimes of zinc phthalocyanine complexes (3 and 4) are also examined in DMSO.

A new fullerene derivative, biindene-C₇₀ monoadduct (BC₇₀MA), was synthesized by [4+2] cyclo-addition reaction between 1,1'-biindene and C₇₀, for the application as acceptor in polymer solar cells (PSCs)⁶⁰. BC₇₀MA is soluble in common organic solvents such as *tetra*-hydrofuran,

chloroform, toluene, *o*-dichlorobenzene, etc., and shows stronger absorption in the visible region and a slightly up-shifted lowest unoccupied molecular orbital (LUMO) energy level than that of PCBM. PSCs were fabricated with BC₇₀MA as acceptor and poly(3-hexylthiophene) (P3HT) as donor for investigating the photovoltaic properties of BC₇₀MA. The power conversion efficiency of the PSC based on P3HT/BC₇₀MA (1:1, w/w) with the additive of 3% octane-1,8-dithiol and thermal annealing at 110 °C for 10 min reached 3.44% with open circuit voltage of 0.64 V, short circuit current of 8.02 mA/cm² and fill-factor of 0.67, under the illumination of AM1.5, 100 mW/cm².

More recently, a facile approach to develop a novel soluble liquid-crystalline fullerene derivative, N-methyl-2-[(4-(4'-cyano)biphenyloxy)hexyloxyphenyl]-3,4-fulleropyrrolidine, C₆₀-bp-CN is reported⁶¹. Compared to C₆₀, the modified C₆₀-bp-CN shows broadened light harvesting and lower LUMO level (-4.2 eV), ascribing to the strong intermolecular interaction induced by self-assembled cyanobiphenyl mesogens, especially after thermal annealing from liquid crystalline states. When blended with poly(3-hexylthiophene) (P3HT), the absorption of the blend film is red-shifted to 700 nm, and the intensity is also remarkably increased. The results indicate that the modified C₆₀-bp-CN is a promising acceptor for polymer solar cells (PSCs) based on BHJ active layers. Therefore, solar cell devices based on an ITO/PEDOT:PSS/P3HT:C₆₀-bp-CN/LiF/Al configuration are fabricated. Clearly, the performances of all the devices are dramatically enhanced relative to corresponding species based on P3HT/C₆₀ active layers. Among all the thermal treatments the *meso*-phase annealing achieves the best performance with a short-circuit current density (J_{sc}) of 5.5 mA/cm², an open-circuit voltage (V_{oc}) of 0.52 V, a calculated fill factor (FF) of 0.23, and a power conversion efficiency (PCE) of 0.65%, which is 3 times higher than that of the untreated one.

Vigilances are going on to modify the structure of parent super-molecules which can be achieved by various functionalizations and these novel molecules may entail an application for solar energy conversation.

Conclusion

Super-molecules are large molecules, composed of subunits with each subunit designed to perform a specific task. A Super-molecule is a single molecule but still it is engineered to act as a complex system. So novel supramolecules, or "molecular devices," can be designed and synthesized that perform their designed function as a result of interaction with light. Novel/modified super-molecules based molecular devices collect electrons when photo initiated. When the subunits of the system absorb photons of light the system is triggered to collect electrons. This allows the conversion of light energy into electrical energy.

"One of the major advantages of photovoltaic is the fact that it is non-polluting, requiring only real estate (and a reasonably sunny climate) in order to function. Another advantage is the fact that solar energy is unlimited. Once a photovoltaic system has been installed, it can provide energy at essentially no cost for years and with minimal maintenance".

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