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A Short Review of Some Examples of the Binding of Fullerenes C60 to Transition Metal Complexes

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Abstract: Fullerenes C60 are molecules composed of carbon atoms arranged in a hollow spherical structure. They have been found to bind to transition metal complexes, which are molecules composed of a metal atom and one or more other atoms. This binding has been found to be very strong, with the fullerene molecules forming a protective shell around the transition metal complex. This has potential applications in a range of fields, such as biochemistry and nanotechnology. This review provides a description of some of the examples of such binding, including the different types of transition metals involved, the binding energies associated and the different structures observed.

Keywords: Fullerenes C60, Metals Involved, Transition Metal, Nanotechnology

I. INTRODUCTION

A. Fullerenes

Observations of interstellar space by radio astronomers suggested the existence of chains of carbon atoms within some stars, the red giants. In seeking to produce conditions close to those existing in these stars to obtain these molecules in the laboratory, H. W. Kroto, R. F. Curl and R. E. Smalley had no idea that they were on the verge of a discovery that revolutionized our certainties about carbon. [1] Indeed, the analysis of carbon aggregates formed within a very hot plasma obtained by vaporizing graphite using a laser revealed the existence of cage-shaped molecules made exclusively of carbon: fullerenes. [2] After graphite and diamond, a third form of pure carbon was discovered. While the other two varieties are solids with infinite lattices of atoms, fullerenes are well-defined molecules. However, the study of these compounds will only be possible a few years after their discovery thanks to the development of a method of synthesis in macroscopic quantities. We will present here this new family of molecules, in particular buckminsterfullerene (named after the architect Buckminster Fuller) or C60 which is the most abundant and most studied representative.

a. Production of fullerenes

The technique for the production of fullerenes was developed in 1990 by Krätschmer and Huffman. [3] This method is based on carbon vaporization under a helium atmosphere.

The experimental device consists of two graphite rods connected to copper electrodes (Figure I-1). One of the rods is cut into a point and kept in contact with the other with a spring. The whole is enclosed in a glass bell equipped with a pumping system to evacuate the air and a helium inlet. When an electric current passes through the graphite rods, the heat of ohmic origin is dissipated mainly at the small point of contact between the two rods. The temperature then reaches 2500-3000°C and the graphite vaporizes into a plasma that cools on contact with the helium atmosphere to form soot. This raw material consists of a mixture of soluble fullerenes (C n, n<100), so-called "giant" fullerenes (C n,n>100), nanotubes and amorphous carbon. By extraction techniques, it is then possible to isolate the soluble fullerenes from the soot. [4] Chromatographic methods are then used to separate the different fullerenes.

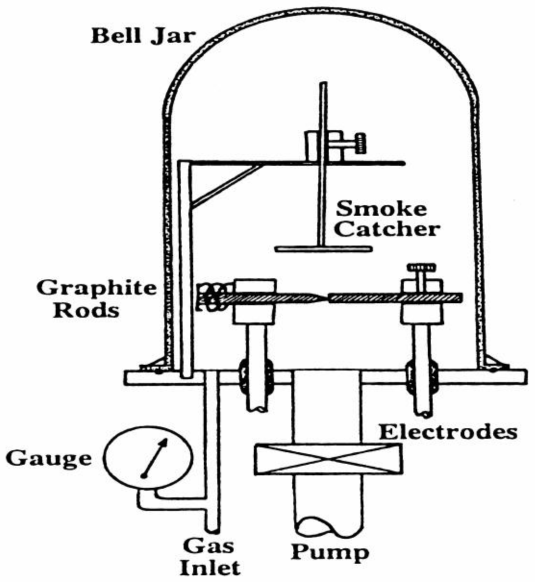

Figure I-1. Experimental device for the production of fullerenes (after A. Hirsch, The Chemistry of the Fullerenes, Thieme, Stuttgart, 1994).

B. Structure of fullerenes

Fullerenes are cage-shaped molecules with 2(10 + n) carbon atoms forming 12 pentagons and *n* hexagons. It was because of its resemblance to the geodesic domes imagined and created by architect Buckminster Fuller that the C_{60} was named Buckminsterfullerene, and the term fullerene was subsequently applied to all representatives of the family. It is interesting to note that the principle of construction of these compounds is a consequence of Euler's theorem: to obtain a polyhedron from a network of n hexagons, it takes 12 pentagons (except for *n* = 1).

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In fact, the smallest fullerene that can be imagined in theory is the C_{20}. From C_{20}, any aggregate consisting of an even number of carbon atoms can form at least one fullerene-like structure. By increasing n, the number of fullerene isomers increases rapidly, from 1 for n = 0 to more than 20000 for n = 29. Buckminsterfullerene (C_{60}) is the smallest stable fullerene. This compound has the shape of a truncated icosahedron, it is in fact the exact replica of a football (Figure I-2). Formed by 12 pentagons and 20 hexagons, each pentagon being surrounded by 5 hexagons, C 60 is a very symmetrical molecule in which all carbon atoms are equivalent. It can also be noted that there are two types of carbon-carbon bonds in this molecule: bonds located at the junction of two hexagons (bonds 6-6) and those located at the junction of a hexagon and a pentagon (bonds 5-6). In fact, links 6-6 are shorter than links 5-6. In other words, 6-6 bonds have a double bond character while 5-6 bonds have a single link character. This localization of π electrons results from the pyramidalization of carbon atoms sp[2] due to the spherical structure preventing a good orbital recovery. C_{60} is therefore not an aromatic molecule.

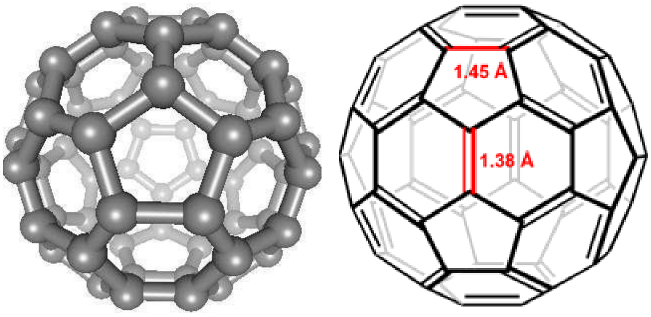


Figure I-2. Structure of C_{60}.

Buckminsterfullerene is the only isomer of C_{60}, it is also the smallest of the fullerenes obeying the "rule of isolated pentagons". The latter predicts that fullerene structures in which all pentagons are isolated by hexagons are more stable than those with two adjacent pentagons [5]. The destabilization related to the presence of two adjacent pentagons results essentially from a high cycle voltage due to the presence of connection angles very far from the standard 120°. The second stable fullerene is C_{70}. Its structure respects the rule of isolated pentagons and it has an oval shape, like a rugby ball. In fact, at its two poles, the structure of the C_{70} is similar to that of the C_{60}. In contrast, the C_{70} has an equatorial belt consisting of fused hexagons (Figure I-3).

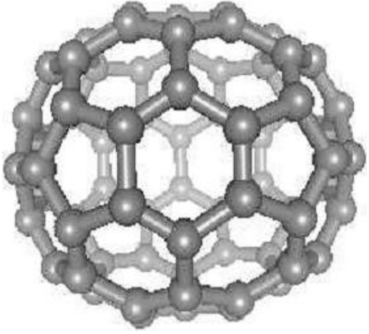


Figure I-3. Structure of the C_{70}.

Considering that only the fullerenes C x that respect the rule of isolated pentagons are stable, the magic x digits are: 60, 70, 72, 76, 78, 84 ... . The number of possible isomers in theory is one for C-60, one for C-70, one for C-72, one for C-76, five for C-78, 24 for C-84 and 46 for C_{-90}. All these fullerenes, with the exception of C_{72}, are actually obtained during the evaporation of graphite under helium atmosphere. To date, a good part of these products has been isolated and characterized.

C. Physicochemical Properties of Buckminsterfullerene

In the rest of the introduction, we will focus only on the case of the C_{60}. It is actually the most abundant of the fullerenes and certainly the one that has been the most studied. It should be noted, however, that the majority of the physicochemical characteristics of C_{60} are found in its higher counterparts.

a. Solubilities

Systematic studies have been conducted to determine the solubility of C_{60} in a wide range of organic solvents. It proved insoluble in polar solvents such as acetone, alcohols, as well as tetrahydrofuran, diethyl ether or dimethyl sulfoxide, poorly soluble in hydrocarbons such as pentane, hexane or cyclohexane. The most suitable solvents for the solubilization of C_{60} remain aromatic solvents such as benzene (1.7 mg/mL), toluene (2.8 mg/mL) or 1chloronaphthalene (51 mg/mL). It can be noted that the solutions of C_{60} have a characteristic mauve-magenta color (Figure I-4).

Figure I-4. A solution of C_{60} in toluene.

The solubility of C 60 in organic solvents, although sufficient to allow its manipulation, was quickly considered too low to consider making devices incorporating pure C_{60}. Another problem lies in the tendency of fullerene molecules to aggregate with each other, which changes their properties. For these reasons, fullerene chemistry has been instrumental in finding reactions to covalently bind solubilizing groups to the carbon sphere.

b. Photophysical properties

Among the quite remarkable physico-chemical properties of C_{60} are the optical nonlinearity and its qualities in terms of optical limitation. [6] Indeed, the absorption of light by C_{60} in the visible range is low if the molecule is illuminated by low light intensities. However, absorption increases considerably when light intensity becomes more important: absorption is non-linear. This phenomenon can be used to protect an optical detector (a camera, the human eye...) against laser aggression without preventing its use under low illumination such as daylight. The C_{60} molecule has a very high symmetry.

Thanks to this symmetry, a theoretical description of the optical properties of the isolated molecule is possible, which makes it possible to explain the non-linear absorption observed experimentally: the theoretical description predicts a much greater absorption for the molecule in an excited level than in its fundamental level. Since the number of excited molecules in a sample directly depends on the incident light intensity, this leads to stronger absorption for high incident intensity. This is called *reverse saturable absorption* (UPS). Several studies of the non-linear absorption of$_{C60}$ have been performed, usually in solution in toluene. The results are interpreted by the ASI as part of a five-level model (Figure I-5).

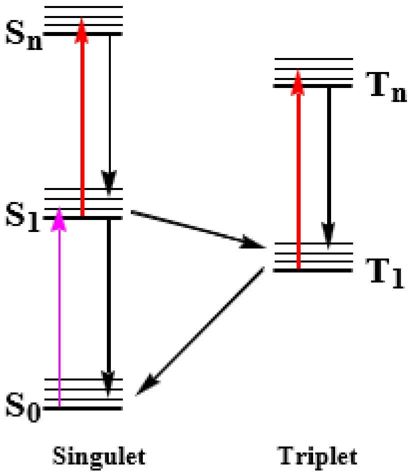


Figure I-5. 5-level model to explain the photophysical properties of C_{60}.

Each electronic level is associated with a large number of vibronic states of the molecule, this greatly expands the absorption domain of the molecule. The vibronic states associated with electronic states are close in energy and partially overlap. In this way, to describe the optical properties, a simplified representation can be used. In this image, the ground state of the molecule and its vibronic levels are associated in an$_{S0}$ level. The entire first group of singular excited states is grouped into an S1 level. Note that the transition S $_0$→S_1 is prohibited by symmetry, so the associated absorption is low. The other singlet excited states of higher energy that cause transitions allowed from the ground state are associated with an Sn level (the first transition allowed is in the near-UV blue, and in the linear absorption spectrum, strong absorption is observed in this spectral zone). The triple states can also be divided into a group T $_1$ and a group T_n. At the level of non-linear absorption, it turns out that some transitions from state S $_1$ to states S_n are allowed in the visible domain. The same applies to transitions between the constituent states of levels T $_1$ and T_n. As a result, a population in an excited state, singlet or triplet, is much more absorbent in the visible than a population in the ground state. If the C_{60} is illuminated by a low light intensity, the population of molecules in the ground state is much larger than that in excited states, because the low intensity generates few transitions that populate the excited level. At higher intensity, the population in the first excited state becomes non-negligible and absorption increases with the population in this excited state, therefore with incident intensity. The absorption induced by a laser pulse can last for microseconds. For the limitation of long pulses, the existence of triplet states is of paramount importance because effective limitation requires an excited population with a lifetime that is at least comparable to the duration of the pulse. Otherwise a balance between absorption S 0-S 1 and relaxation S 1-S_0 is established during a long pulse. The average excited population during the pulse will be low and, accordingly, the limitation too. A key parameter in the case of long pulses is the rate of molecules that perform intersystem transfer and accumulate in the T1 level, instead of de-exciting directly. The higher the rate, the more effective the limitation will be for long pulses that require the presence of a triplet population with a sufficiently long lifespan. In this perspective, the C $_{60}$ appears to be a good candidate because in solution in toluene, the intersystem crossing is done with a yield close to unity.

c. *Electrochemical properties*

Theoretical calculations[7] had predicted that the$_{C60}$ molecule possessed an unoccupied molecular orbital triply degenerate quite low in energy. In simpler terms, this molecule should have an electron acceptor character and, in principle, could accept up to 6 electrons to form a $C_{60}{}^{6-}$ hexaanion. As soon as pure samples of$_{C60}$ were obtained, the electrochemical properties were studied and the theoretical predictions were verified experimentally. Indeed, it has been shown that C_{60} could accept up to 6 electrons by six successive monoelectronic reductions (Table 1). [8] It should be noted, on the one hand, that all these reductions remain reversible processes and, on the other hand, that the anions obtained are stable for several days at low temperatures. Emphasize also that if the C 60 is relatively easy to reduce (at least for the first reduction leading to the $C_{60}{}^{-}$ anion), it is rather difficult to oxidize it.

Table I-1. Reduction potentials obtained at -10°C in a CH_3CN / toluene mixture.

Monoelectronic torque	Reduction[h]
C 60/C 60	- 0.98
C60 -/C602 -	- 1.37
C 602 -/C603 -	- 1.87
C 603 -/C 604 C	- 2.35
604 -/C 605 -	- 2.85
C 605 -/C606 -	- 3.26

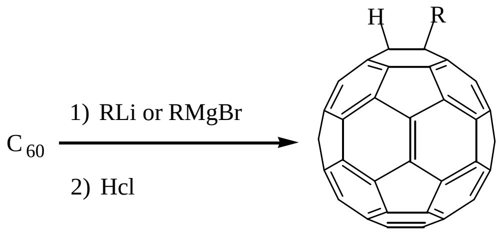
[a] potential values, in V (*vs*. Fc+/Fc), obtained for a scanning rate of 100 mV.s-1.

These results are particularly important because they offer a first indication of the chemical reactivity of$_{C60}$. Indeed, the electronegativity of C_{60} suggests that this molecule will rather be an electrophile that can be the seat of addition reactions by attack of a nucleophile.

II. CHEMICAL PROPERTIES OF BUCKMINSTERFULLERENE

Since the development in 1990 of the process of synthesis of macroscopic quantities ofC_{60}, its chemical reactivity has been the subject of numerous studies. Reactions to graft groups onto the surface of C60 have been discovered and, to date, a large number of C60 derivatives have been produced. The chemical modification of C_{60} has a first interest, that of considerably increasing its solubility after grafting. This makes derivatives much easier to handle. On the other hand, many groups with a specific function could be grafted onto C_{60} to obtain molecules with original properties. It is impossible to summarize all these works in a few pages and we refer the reader wishing to obtain more information to two books dealing with these aspects in detail. [9] [10] We will confine ourselves here to giving some examples of chemical reactions
allowing to graft a group on the C_{60}.

C_{60} has a chemical reactivity similar to that of an electron-deficient olefin. Thus, C_{60} is a good electrophile and can be the seat of nucleophilic addition reactions. C_{60} reacts for example with different nucleophilic derivatives such as organoliths or organomagnesians. The corresponding salts C 60 RM generated rapidly by addition of the organometallic on C 60 can then be protonated in an acid medium to achieve the corresponding hydroalkyl or hydroaryl derivatives (Figure I-6).



R = Me, and, *i*-Pr *t*-Bu, Ph

Figure I-6. Nucleophilic addition of organolithic or organomagnesian on C_{60} followed by acid hydrolysis.

A cyclopropanetrione reaction of C_{60} by an addition/elimination mechanism was demonstrated (Figure I-7). This involves the reaction of a stabilized α-halocarbanion with C_{60}. The mechanism of this reaction can be divided into two steps: first, C_{60} is the site of a nucleophilic attack by α-halocarbanion generated by reaction of a base (NaH) with α-bromo-malonate. The second step is a substitution intramolecular nucleophilic to generate the cyclopropanation product.

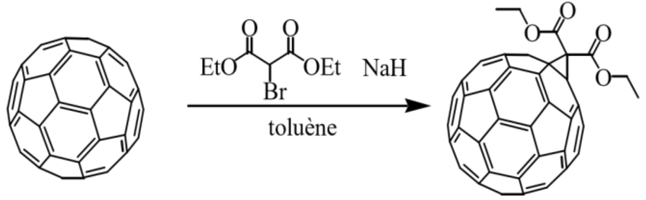


Figure I-7. Cyclopropanation of C_{60}.

C_{60} can also play the role of dienophile or 1,3-dipolarophile (Figure I-8). Thus, cycloadditions of all types leading to the synthesis of cyclic derivatives are possible: namely, [2 + 1] cycloadditions of carbene or nitrene insertion type, cycloadditions [4 + 2] type Diels-Alder, cycloadditions [2 + 2] thermally or photochemically induced, or cycloadditions [3 + 2] 1,3-dipole (Figure I-8).

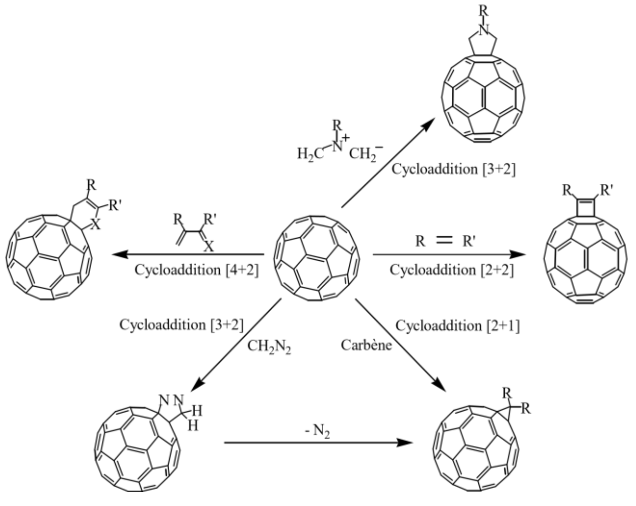


Figure I-8. Different cycloaddition reactions involvingC_{60}.

These different reactions developed during the first years after the discovery ofC_{60} were used to prepare many derivatives, initially carrying solubilizing groups, then, increasingly, also carrying functional groups for the creation of original materials.

III. ASSOCIATION OF C60 WITH ELECTRON AND/OR ENERGY DONORS

A whole field of fullerenes chemistry has been dominated in recent years by the desire to associate the excellent acceptor that is C_{60} with donors of different types, in order to form donor-acceptor dyads likely to give rise to photoinduced electron transfer phenomena. In addition, the first excited singlet and triplet states of C_{60} are relatively low in energy, so fullerenes are also good candidates for photoinduced energy transfer. [11][12] Thus new molecular dyads composed of an electron or energy donor capable of photoinduced electronic or energetic transfer to the C60 acceptor are now widely studied. [13] This type of research has motivated a great deal of work that cannot be listed exhaustively. [14][15][16][17][18][19] We shall therefore confine ourselves to quoting here.
chromophores that have been most commonly associated withC_{60}.

A. C60-porphyrin dyads

C-$_{60}$/metalloporphyrin dyads constituted the bulk of the first studies on electron and energy transfer processes between metal complexes and$C$-$_{60}$. The great efforts invested in the development of such systems are partly due to the mimicry of their behavior with the process of photosynthesis. [20] In 1994, Gust and his collaborators[21] were the first to synthesize a system combining the two chromophores covalently (Figure I-9). In addition, they also showed that these dyads were photoactive compounds that could give rise to energy or electron transfers after
photoexcitation.

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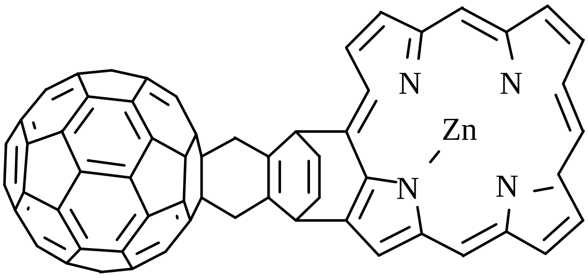
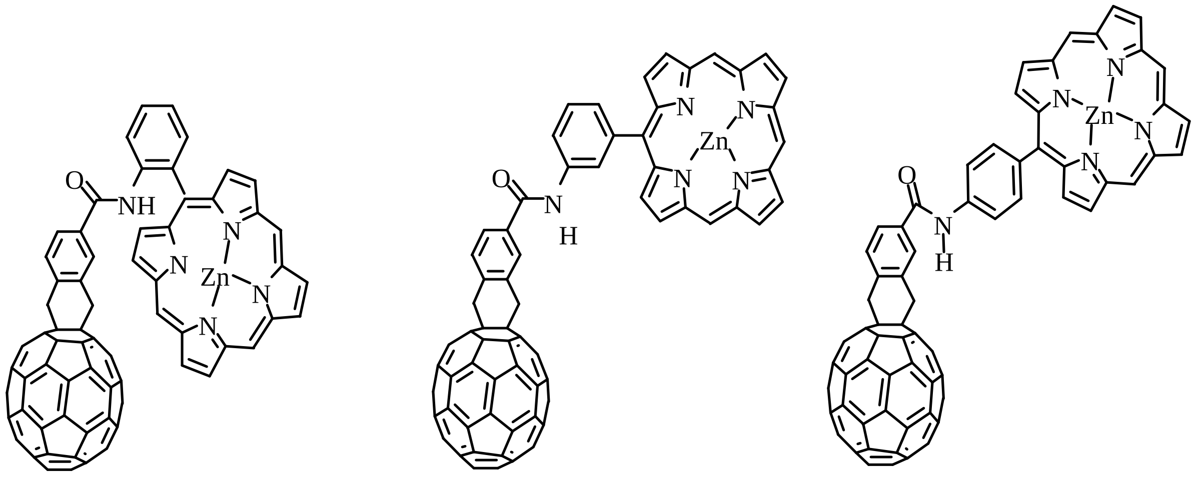


Figure I-9. First C60-metalloporphyrin dyad.

Subsequently, Imahori and colleagues[22] prepared and studied 3 dyads differing from each other only in the relative position of C_{60} and porphyrin (Figure I-10). The modification of the bridge connecting the two photoactive parts then made it possible to emphasize the influence not only of their nature but also of the relative position it imposes on the two chromophores. They then observed that the photoinduced charge transfer was all the faster as the two photoactive parts were close. Thus, the rate constant of charge transfer of the *meta* compound is lower than that of ortho and *para* compounds. These measurements reflect the stronger electronic interactions existing between the chromophores of these last two products compared to that of the *meta* product.



Ortho ***meta*** ***para***

Figure I-10. Ortho, meta and para isomers of a C 60-metalloporphyrin dyad.

The influence of the nature of the bridge has also been highlighted many times. The work of Wilson and his collaborators[23] on 3 dyads where C_{60} is connected to porphyrin by a steroid with respectively 0, 1 and 2 double bonds are very interesting (Figure I-11). In this study, the choice of a rigid bridge makes it possible to exclude any possibility of rapprochement between the two chromophores. Differences in behavior were then observed: the trapping of the excited state of the complex increases with the number of double bonds contained in the bridge.

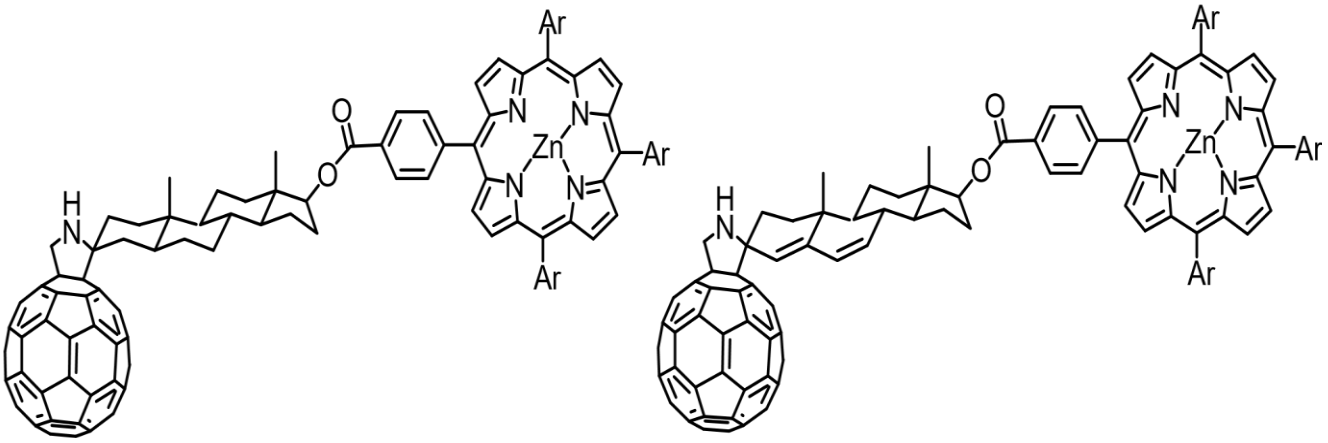


Figure I-11. C-60-porphyrins with rigid bridge, with or without double bonds.

Since electron transfer has been observed and the governing factors better understood, the usefulness of such systems in materials chemistry remains to be demonstrated. A first answer is provided by the processes observed by Imahori [24] on monolayers formed by self-assembly of dyads on a gold electrode (Figure I-12).

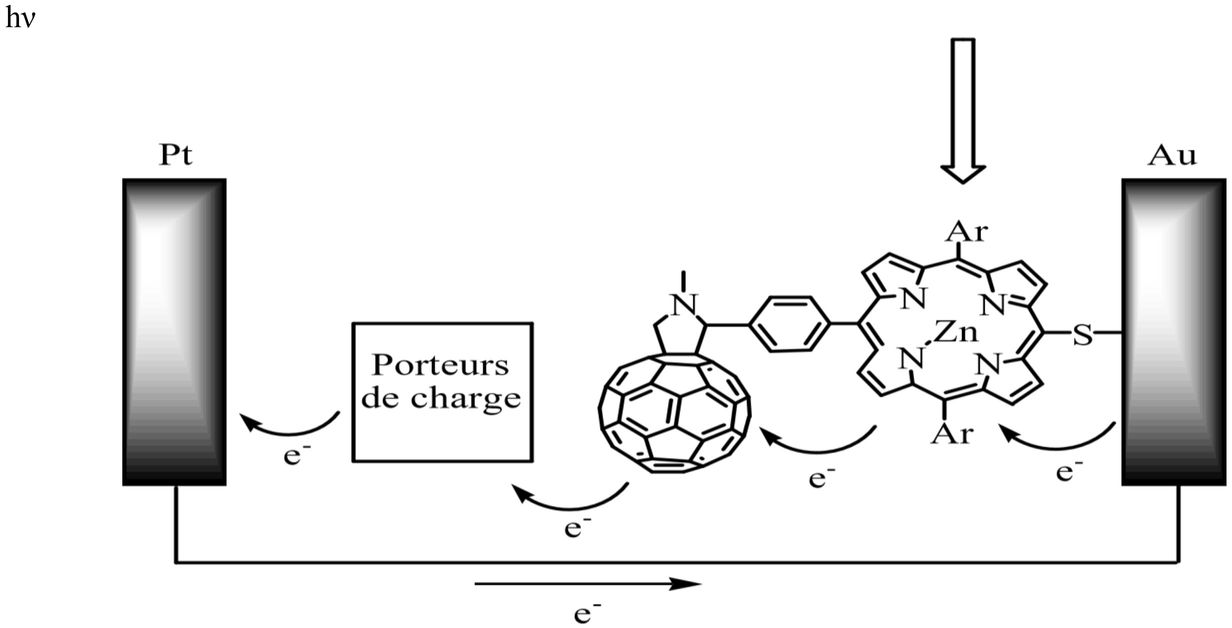


Figure I-12. Self-assembled monolayer of C_{60}/metalloporphyrin dyads generating a photocurrent.

In the presence of charge carriers, a cathode photocurrent was measured after photoexcitation. In addition, the interest of the presence of C_{60} in this type of system seems obvious since the intensity of the current measured for an analogous system does not include of C_{60} is five times lower.

Other more complicated systems have emerged, where attempts have been made to multiply donor chromophores, such as the multiporphyrinic fullerenes of Gust and Aida. [25] One of the advantages of such systems is to mimic natural photosynthetic systems, where many porphyrins capture light energy before redirecting it to the reaction core. This antenna effect is particularly useful for optimizing the absorption of a maximum of photons in the visible domain.

B. C-60-transition metal dyads

Metalloporphyrin/C-60 dyads constitute the majority of work on donor-acceptor systems involving both C-60 and metals. But other systems are now being used more and more frequently. This is the case of transition metal complexes having a *Metal-Ligand Charge Transfer* (MLCT) band. [26] In fact, the excited MLCT states of these compounds have a strong reducing character. This is why they appeared quite naturally as ideal partners of the C_{60} for the purpose of developing donor-acceptor materials. In 1995, Prato et al. [27] studied a dyad in whichC_{60} is connected to a ruthenium complex by an ethylene glycol chain (Figure I-13).

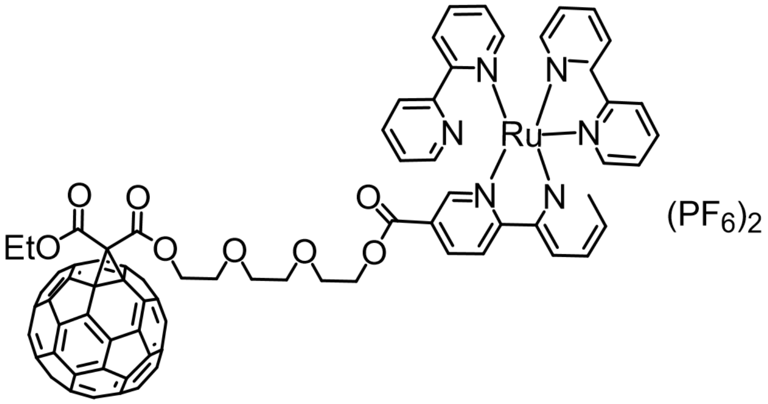


Figure I-13. Dyad C_{60}/Ru with flexible bridge.

They observed a trapping of the excited MLCT state of ruthenium caused by a charge transfer from the complex to fullerene. From then on, several products were prepared according to the same model in order to better understand the influence of parameters such as stiffness, bridge length or the number of chromophores. By inserting a rigid bridge between the C_{60} and the complex, Guldi and his collaborators[28] removed any conformational freedom between these two parts (Figure I-14). Trapping of the MLCT excited state of this compound due to charge transfer was also observed. The rigid bridge allows an efficient separation of loads: indeed, whatever the solvent, the rigidity keeps the C 60 of the complex at a distance, which favors the long life of the state with separate loads.

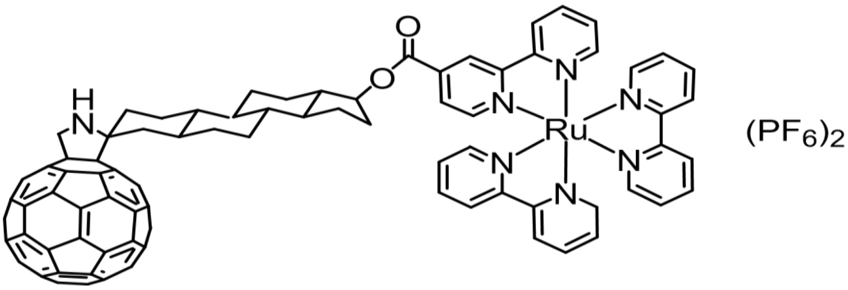


Figure I-14. Dyad C_{60}/Ru with rigid deck.

Various possibilities have been explored to improve the efficiency of burden shifting. The variation of the distance between the two photo and electroactive groups is one of them. By choosing a bridge of polypeptide nature (Figure I-15), Guldi and his collaborators [29] controlled the existence of electron transfer via the nature of the solvent. In chlorobutane, the excited MLCT state of the ruthenium complex is trapped by fullerene resulting in a separated charge state Ru^{3+}-$C_{60}^{\cdot -}$. But by adding a protic solvent, the helical structure of the polypeptide chain becomes disorganized with the consequence of moving away from the two active centers. In this situation, no load transfer is observed. Note also that this situation is perfectly reversible when the protic solvent is evaporated.

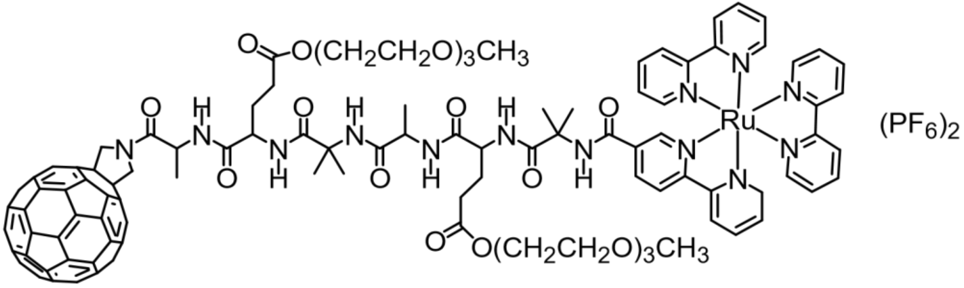


Figure I-15. C-60-Ru(II) complex dyad where the two entities are separated by a peptide bridge.

The multiplication of photoactive centers (metal or C 60) is a concept a priori attractive in order to develop the interactions between C_{60} and metal. This is why Guldi and his collaborators[30] prepared a compound with two metal cores (Figure I-16). The addition of a metal center compared to the compound presented Figure I-14 considerably modifies the nature of the interactions between C_{60} and the metal complex. Certainly, a trapping of the excited MLCT state of the complex is always observed but it is in this case the result of an energy transfer. Indeed, the presence of a second metal center lowers the energy level of the MLCT excited state of ruthenium and makes thermodynamically unfavorable a photoinduced electron transfer.

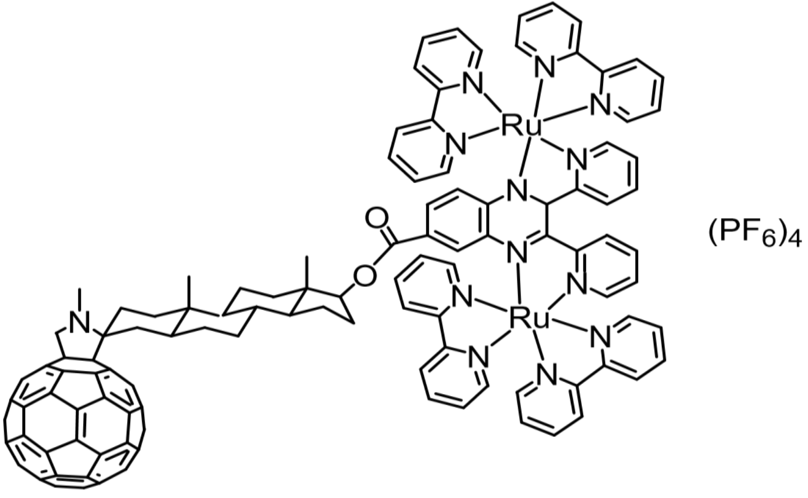


Figure I-16. Dyad C_{60} /Ru with two metal centers.

The influence of the energy levels of the excited state MLCT of the metal complex on the photoinduced processes highlighted in particular in the previous example led to an interest in other metals. Nierengarten et al. [31] compared the photophysical properties of two similar complexes with different metal centers, ruthenium and rhenium (Figure I-17). For both complexes, trapping of the MLCT excited state of the metal complex is observed at room temperature due to electron transfer from the metal to C_{60}. Also in both cases, the lifetime of the separated charge state is very short due to rapid recombination of charges to the first triplet excited state of fullerene. Some differences nevertheless appear depending on the metal: thus in a rigid matrix (ie at 77K in a medium of composition CH 2 Cl_2 / MeOH 1: 1), The rhenium complex gives rise to a photoinduced electron transfer while no photophysical phenomenon is observed for the ruthenium complex. In fact, the transition from the solution to the frozen matrix prevents the reorganization of the solvent after electron transfer and destabilizes the species with charges separated by about 0.5 eV. Thus, the photoinduced electron transfer becomes thermodynamically unfavorable in the case of the ruthenium complex while the process remains favorable for the rhenium complex.

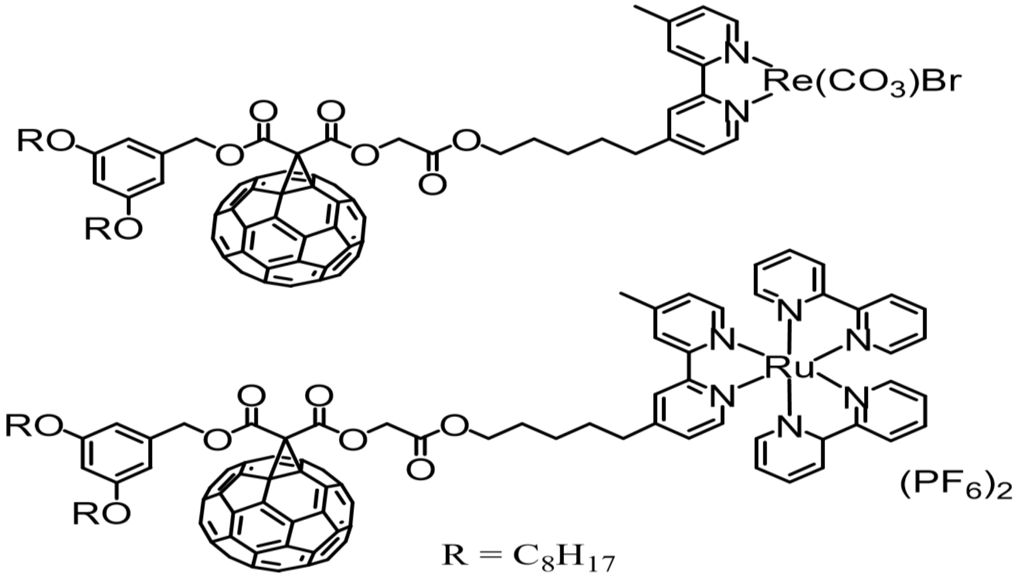


Figure I-17. Ruthenium and rhenium complexes of a$_{\text{C60-bipyridine}}$ ligand.

The problem posed by these complexes for practical applications lies in the rapid deactivation of the state with separate charges (~1.95 eV) to the first triplet excited state of C_{60} (~1.40 to 1.50 eV). It therefore becomes necessary to develop compounds with a separate charged state energy level approaching 1.40 eV in order to avoid this rapid recombination by reducing the ΔG of the process, assuming that the process is in the normal Marcus region. This assumption is reasonable because of the low ΔG value of this recombination of charges via the triplet excited state of C_{60}. In this

In perspective, attention should be paid to the copper(I) complexes of 1,10phenanthroline[32] whose photophysical and electrochemical properties are more compatible with these requirements. Nierengarten and colleagues explored this combination by performing molecular assemblies associating fullerene with copper(I) complexes of 1,10-phenanthroline (Figure I-18). [33] Photophysical properties have shown that the MLCT excited state of the copper(I) complex is trapped by an electron transfer process to C_{60}. The energy level of the state with separate loads is about 1.50 eV, so that the recombination of charges to the first triplet excited state of C_{60} (1.40 eV) is sufficiently slowed down to no longer compete with the direct return to the ground state. Similar results were also observed in the photophysical study of the copper(I) complex of a rotaxane with C60 caps[34].

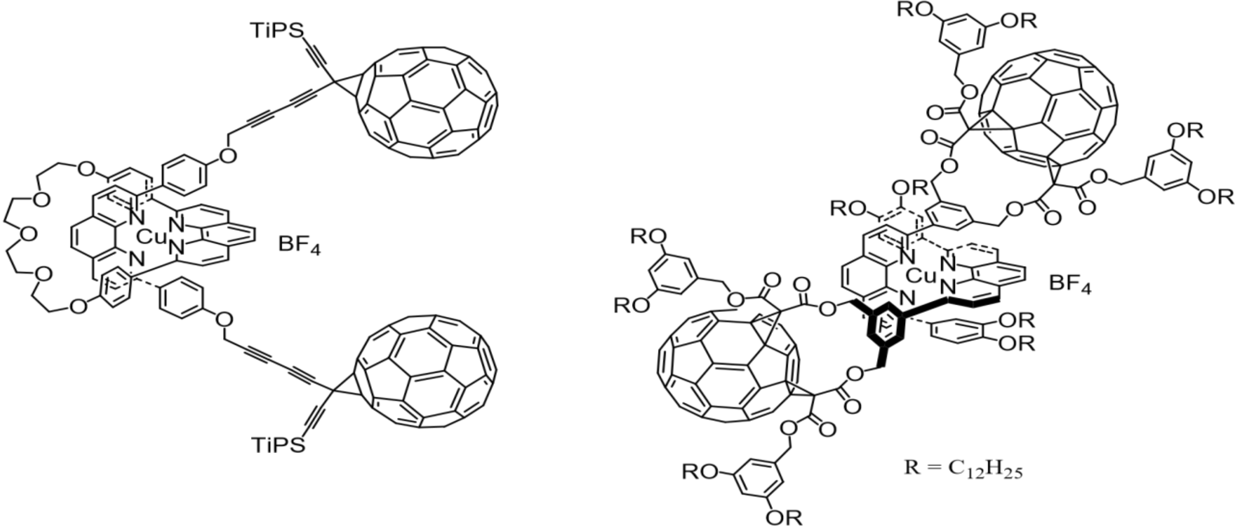


Figure I-18. Rotaxane Cu/C 60 (Jean-Pierre Sauvage and collaborators) and Cu/C_{60} complex developed in the laboratory.

C. C-60-π-conjugated systems

Many research teams have also been interested in the preparation of C-60 donor systems with π-conjugated oligomers as donors. The great interest in the use of π-conjugated systems is in their semiconductor character associated with a completely conjugated structure capable of easily transporting loads. [35]

So it is not surprising that very varied π-conjugate systems such as derivatives of oligo(thiophene), [36] oligo(p-phenylenevinylene), [37] oligo(phenylene-ethynylenes), [38] oligo (thienylene vinylenes), [39] oligo(thienylene ethylenes),[40] oligo(naphthalenes) [41] etc... were covalently linked to the sphere of$_{C\text{-}60}$ (Figure I-19).

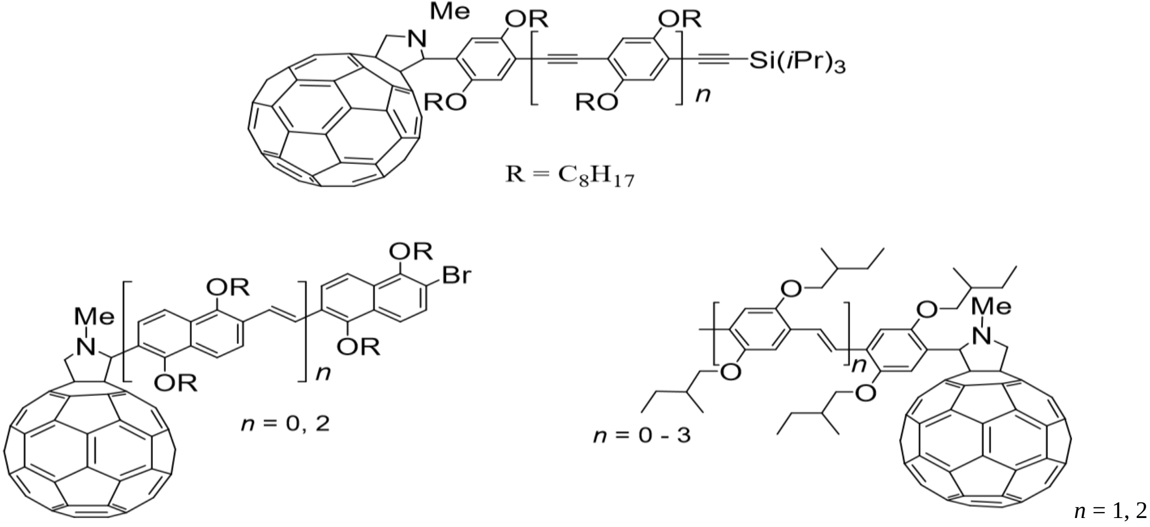


Figure I-19. Examples of oligomeric π-conjugated systems -C_{60}.

Many studies have established that the process of photoinduced electron transfer in this type of system is in competition with an energy transfer process.[41] Similarly, it has been shown that those two processes are or can be controlled by the nature of the solvent. For example, the work of O. Ito et al. [42] who studied the influence of solvent polarity on photoinduced processes within an oligo(thiophene)-C60 system (Figure I-20). If an extremely fast energy transfer is observed from the singlet excited state of the conjugate system to C 60 in all solvents, the deexcitation of the first singlet excited state of C_{60} thus obtained strongly depends on the polarity of the solvent. In fact, in nonpolar solvents such as toluene, the separately charged state is higher in energy than the singlet excited state of$_{C60}$ and electron transfer is not possible. On the other hand, in more polar solvents such as THF or benzonitrile, the state with separate charges is lower in energy and electron transfer is possible. This has indeed been observed and the quantum efficiency of charge separation is close to unity.

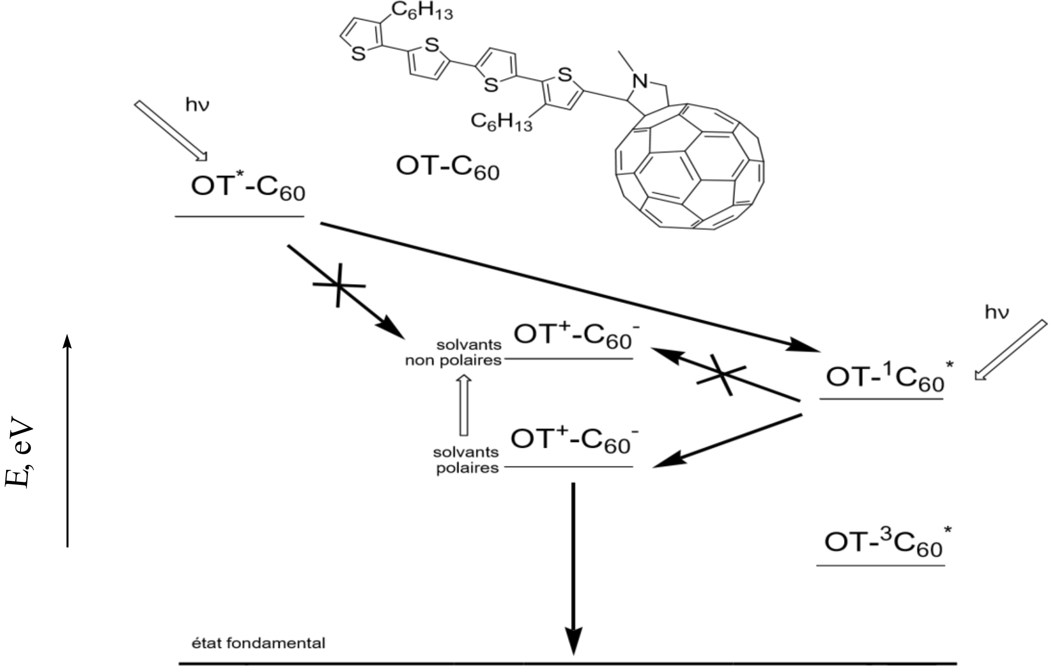


Figure I-20. Energy level diagram describing photoinduced phenomena as a function of the nature of the solvent.

Similar effects were observed for oligo(thiophenes)-C 60[36] and oligo(p-phenylenevinylenes)-C_{60} systems. [37] It should also be noted that it is possible to increase the donor character of the conjugated system by functionalization with an amine group. [43] In this case, the energy level of the separately charged state is lower than that of the first singlet excited state of C_{60} and electron transfer is observed regardless of the nature of the solvent. [38]

The process of electronic transfer in$_{C60}$ conjugated oligomer systems has resulted in [44] applications in the field of conversion of light energy into electrical energy (photovoltaic effect). [45] [57] [60] This phenomenon involves the production of electrons (negative charges) and holes (positive charges) under the effect of light in the semiconductor material.

Recently, a new concept based on the use of a thin film of a mixture of a conjugated polymer and C_{60} has been proposed and has significantly optimized the performance of plastic photovoltaic devices using organic compounds, but many obstacles remain to be overcome before a possible application. In particular, the performance of the device is a function of the morphology of the thin film and one of the major problems is the incompatibility of the two constituents of the mixture. This results in an uncontrollable phase separation limiting the performance of the photovoltaic device since the photoinduced charge separation at the origin of the photocurrent can only be done at the C_{60} / polymer interface (contact zone between the two constituents). In order to eliminate all the problems resulting from this phase separation and to obtain a mixture as homogeneous as possible, Nierengarten and his collaborators had proposed to covalently bind the conjugate system to the C_{60} molecule. [46][53][58] For example, compound $C_{60\text{-}3PV}$ was used for the preparation of photovoltaic cells (Figure I-21).

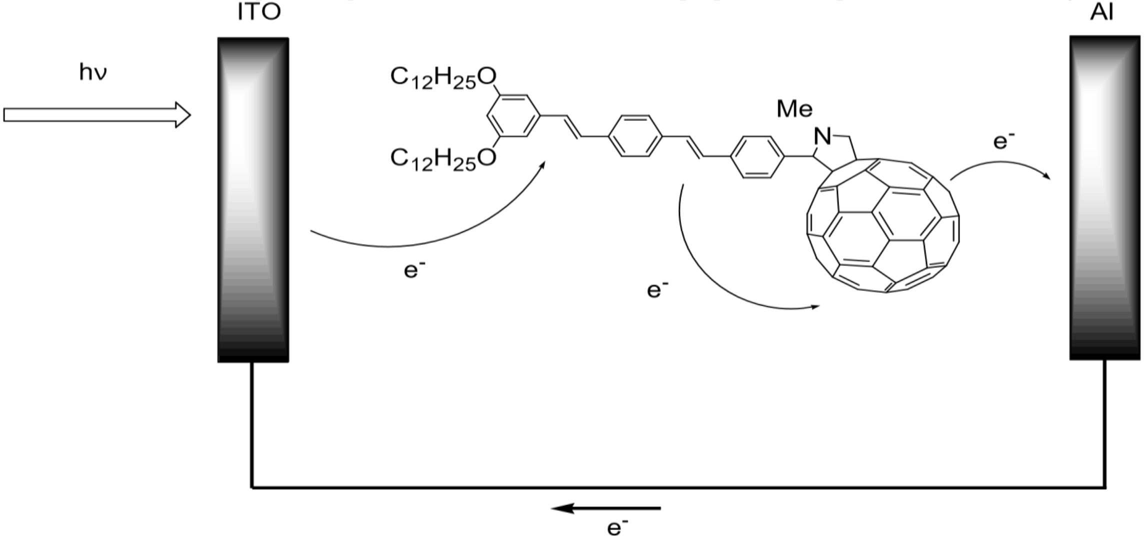


Figure I-21. Compound C 60-3PV and schematic representation of the photovoltaic device.

In such a device, compound **C 60-3PV** is not only able to generate electrons and holes, but it also provides paths for their transport to the two opposite electrodes and a photocurrent is obtained. This molecular approach to the conversion of solar energy into electrical energy is particularly original. Since the publication of this result in 1999, many molecules combining C_{60} with conjugated systems have been used for the development of photovoltaic devices. All the results obtained also show the advantage of the molecular approach, which makes it possible to establish a structure/activity relationship and to easily vary the structure of the fullerene-donor system to modulate its electronic properties. [47]-[60]

IV. CONCLUSION

This thesis work has demonstrated that covalent systems combining C_{60} and transition metal complexes with a charge transfer band from the metal to the ligand can be successfully synthesized. Furthermore, by exploring different geometries and structures, this allowed for an overview of the photo physics of compounds resulting from the association of C_{60} with this type of complex. Additionally, this work explored the possibility of supramolecular associations between fullerene derivatives and chromophores oligophenylene vinylene to create photoactive supramolecular structures. Overall, this thesis work has provided insight into the potential of C_{60}-based systems for photophysical applications.

DECLARATION

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Authors Contributions	I am only the sole author of the article.

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