FULLERENES, HIGHER FULLERENES, AND THEIR HYBRIDS: SYNTHESIS, CHARACTERIZATION, AND ENVIRONMENTAL CONSIDERATIONS

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1.1 INTRODUCTION

The search for alternative and renewable energy sources has become one of the major thrusts of the twenty-first-century researchers due to the increasing demand for energy. Innovations and development of photovoltaics, dye-sensitized or polymer solar cells, high-efficiency lithium ion batteries, supercapacitors, transparent conductors, hydrogen productions and storage systems, microbial fuel cells, catalyst-driven proton exchange membrane fuel cells, thermoelectric power generation, etc., have come to the forefront in alternative energy research [80, 149]. In quest of effective energy transfer, distribution, and storage, improved materials are being synthesized since the 1990s. Nanoscale manipulation of materials has fueled such development [11]. Improved surface area at the nanoscale and targeted molecular placement or alteration in nanomaterials resulted in desired band gap tuning and effective electron transfer, storage, and surface activity [111]. One of the key challenges that eluded energy researchers for decades was an efficient photoelectron acceptor with high structural stability and chemical reactivity; a spheroidal...
carbon allotrope, known as fullerene, addressed this critical gap in alternative energy research and development [31, 111].

Sixty carbon atoms, organized following isolated pentagon rule (i.e., 20 hexagons and 12 pentagons), forming a truncated icosahedron structure is known as buckminsterfullerene—the first member of the fullerene family, discovered by Sir Harry Kroto, Robert Curl, and Richard Smalley in 1985 [136]. Fullerenes’ ability to effectively function in donor/acceptor heterojunctions has popularized its synthesis, derivatization, and supramolecular assembly for photovoltaic applications [31]. Later, detection and effective isolation of higher-order fullerenes [121], that is, C_{70}, C_{76}, C_{82}, C_{84}, etc., have encouraged their studies and uses in energy applications. Changes in hole/electron-pair generation ability and electronic band gap with the changing number of atoms in the fullerene structures have continued to evoke interest in these higher fullerenes [61, 169]. Electronic structure could be further tuned by conjugation of fullerenes with other carbon allotropes, for example, carbon nanotubes (CNTs), graphene, etc., which has encouraged synthesis of hierarchical assemblages of fullerenes with other nanoscale structures, resulting in nanoscale hybrid (NH) materials [3, 146, 201, 212, 272].

C_{60}s, especially its polymeric derivative [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM), has been known to be the most effective electron acceptor for organic photovoltaics [31]. Recent advances in this field have proposed a novel donor/acceptor blend for hole/electron transfer. By photoexciting the donor, electron moves from the lowest unoccupied molecular orbital (LUMO) of the donor to the acceptor, where the hole gets transported to the donor. C_{60}’s excellent electron-accepting ability has presented it as an ideal candidate for photovoltaic solar cell construction. Their applications in organic field-effect transistors [9] and lithium or hydrogen storage [42] also depend on its high electron affinity and high charge transferability. C_{60}s also act as promising catalytic composites and electrode materials for Nafion-based proton exchange membrane fuel cells [243]. Similarly, higher-order fullerenes such as C_{70}, C_{76}, C_{84}, and C_{90} and their derivatives are also being utilized as higher-efficiency transistors and have shown promising solar cell efficiencies [128, 221, 244]. Moreover, hybridization of fullerenes to formulate concentric fullerene clusters or carbon nano-onions [90], fullerene nanopeapods [146] or nanobuds (fullerene–CNT hybrids) [245, 255], and endohedral metallofullerenes [263] enhances their promises in energy storage devices. However, such demand of fullerenes requires higher quantity to be synthesized and purified. Such high demand for this material requires unique synthesis and preparation processes, which in conjunction with fullerenes’ inherent attributes can invoke toxic responses to the environment, hence necessitating careful consideration [200].

C_{60} and its derivatives such as C-3, fullerol C_{60}(OH)_{24}, bis-methanophosphonate fullerene, tris carboxyl fullerene adduct tris-C_{60}, dendritic C_{60} monoadduct, malonic acid C_{60} tris adduct, etc. are found to be responsible for inducing toxicological impacts in soil and aquatic microbes [41, 73, 114, 151, 259], invertebrates [276], and fish [276] as well as in human cell lines [78, 196, 205] and rats and mice [71]. Such environmental and biological toxic potentials are known to have resulted from fullerenes’ ability to penetrate cell membranes and generate oxidative stresses. Similarly,
C\textsubscript{70} have also shown to adversely affect aquatic species, when C\textsubscript{70}–gallic acid derivative at less than quantifiable concentration causes significant reduction in *Daphnia magna* fecundity after 21-day exposure. It has also demonstrated generation of oxidative stress through inhibition of enzymatic activities [211]. The demonstrated toxicity of fullerenes resulted in systematic evaluation of its fate, transport, and transformation in natural environment, which include fundamental aggregation [164], deposition and transport in porous media [270], photoinduced transformation [104], etc. C\textsubscript{60} synthesized using different techniques [32, 150], have been studied to evaluate role of synthesis on their potential risk. However, very few studies have focused on systematic investigations of higher fullerenes and fullerene-based NH’s fate, transport, transformation, and toxicity [2, 3, 200, 201].

This book chapter discusses synthesis, characterization, and application of fullerenes, higher fullerenes, and their NHs. The chapter will identify potential risk of these carbon allotropes when used in energy applications and discuss possible strategies for pursuing green synthesis of these materials. The discussion in this chapter will potentially highlight the relevant risk of using fullerenes in energy applications and help establish an understanding of environmental considerations.

1.2  FULLERENE, HIGHER FULLERENES, AND NANOHYBRIDS: STRUCTURES AND HISTORICAL PERSPECTIVE

1.2.1  C\textsubscript{60} Fullerene

C\textsubscript{60} fullerene is an all-carbon and perfectly symmetric molecule made from 60 carbon atoms (Fig. 1.1a). It was the first ever discovered regular truncated icosahedral molecule [197, 242]. The carbon atoms on the vertices of the polygons in C\textsubscript{60} possess $sp^2$ hybridization and become bonded through 6:6 double bond between hexagons and 6:5 bonds between hexagons and pentagons [87]. One carbon atom is bonded to 3 other carbon atoms with a bond length of 0.14 nm. The total spherical diameter of a C\textsubscript{60} molecule becomes 0.71 nm, giving rise to the perfect symmetric cage [95]. Though such molecules possess high structural stability [162, 197, 228, 242], these were found to be highly reactive, where acceptance of electrons makes them strongly reductive [99, 100]. Such conjugate reactivity and structural stability help them to produce various derivatives as shown in Figure 1.1b.

The discovery of fullerene was rather extraordinary [130]. A research lab in Exxon group in 1984 had first seen carbon soot presenting similar time of flight (TOF) mass spectra for even numbers of carbon atoms starting from 40 to 200 [198]; however, they were unable to identify the abundance of C\textsubscript{60} in that mixture. In similar time frame, while searching for the mechanism of interstellar long-chain carbon molecule formation, an unusual TOF spectral signature of carbon soot was observed by Sir Kroto, Smalley, and Curl while synthesizing carbon soot through laser irradiation of graphite [136] at Rice University in 1985. The group hypothesized that the spectral signature was generated due to the formation of C\textsubscript{60}, the probable aromatic icosahedron structure with remarkable stability. Later on, nuclear magnetic resonance (NMR)
experiments were performed to conclude that the molecules obtained by Kroto and others truly resulted in C\textsubscript{60} molecules [230]. Kratschmer, Huffman, and Fostiropoulos, on the other hand, came up with synthesis technique for macroscopic amount of C\textsubscript{60} and C\textsubscript{70} in 1989 [132]. In 1995, Harry Kroto, Richard Smalley, and Robert Curl were awarded Nobel Prize in Chemistry for the discovery of C\textsubscript{60}. The aforementioned scientists later named the first discovered carbon allotrope as “buckminsterfullerene” or “fullerene” to pay homage toward the renowned American architect Buckminster Fuller, who designed geodesic dome-shaped structures resembling fullerenes.

### 1.2.2 Higher Fullerenes

Members of fullerene family possessing more than 60 carbon atoms are known as higher-order fullerenes (Fig. 1.1c). They are generally found in the same carbon soot obtained during C\textsubscript{60} synthesis. C\textsubscript{70}, being the first member of the higher-order fullerene family, is always found in abundance with the C\textsubscript{60}s. However, the other members, that is, C\textsubscript{76}, C\textsubscript{78}, C\textsubscript{84} and C\textsubscript{92} (up to fullerenes with more than a hundred carbon atoms), are found in much smaller quantities in the soot. Diederich \textit{et al.} first
found mass spectroscopic evidence for existence of C_{76}/C_{78} and C_{84} and isolated them through extraction technique employment during reproduction of the Kratschmer method for producing C_{60} and C_{70} fullerenes [59]. During the same time, theoretical prediction of their existence, isomerism, and chemical stability was presented by Fowler and Manolopoulos [20, 74, 155, 156]. With the help of the newer chromatographic techniques, fullerenes with a wide range of composition, that is, C_{20} to C_{400} were extracted, isolated, and characterized alongside with identification of isomeric forms of several higher-order fullerenes [121, 189, 214].

1.2.3 Fullerene-Based Nanohybrids

When C_{60} and higher fullerenes are conjugated either exohedrally or endohedrally with carbon- and metal-based nanomaterials, the ensemble materials are known as fullerene-based nanohybrids (NHs) (Fig. 1.1d) [3, 201]. The overall scope of this book will limit the discussion to carbon NHs only. Endohedral NHs can be formed via fullerene and higher fullerene encapsulation within CNTs and larger fullerene structures. These structures are called peapods [218] and carbon nano-onions [219], respectively (Fig. 1.1d). Nanopeapods, prepared in 1998 by Luzzi et al., was one of the first NHs synthesized [218]. Growing interests in fullerene and NH chemistry encouraged development of other NH assemblages, either with CNTs [174] or graphene [194]. The conjugation is performed using both nonspecific short-ranged interaction [257] and via covalent bonding [148, 174] with the use of functional linking molecules or polymers.

1.3 SYNTHESIS AND CHARACTERIZATION

1.3.1 Fullerenes and Higher Fullerenes

Commercial production of C_{60}s and higher fullerenes involves a two-step process [63]. First, carbon soot containing fullerene mixtures is synthesized via carbon vapor generation methods. Second, fullerene separation and purification from the carbon soot are performed to obtain individual fractions of the carbon allotropes. Based on the raw materials and precursors, vaporization methods, and processing techniques, various soot generation processes have been developed. Most of the synthesis techniques were developed during the 1985–1995 time line, when fullerene discovery and techniques for primary isolations and separation were innovated [130]. Later, chemical synthesis processes to form fullerenes from aromatic hydrocarbons were developed [207]. A brief discussion on the major fullerene and higher fullerene production techniques is described in this section. Figure 1.2 shows a flow diagram demonstrating steps involved in carbon soot synthesis and fullerene extraction and purification.

1.3.1.1 Carbon Soot Synthesis

**Arc Vaporization Methods**  Arc vaporization methods are the most effective ones for carbon soot synthesis. The process of resistive heating of graphite rods in helium environment, developed by Kratschmer et al., was the first step to produce carbon
soot containing fullerenes in macroscopic amounts [131]. The method was furthered into AC- or DC-arc-based carbon vaporization processes to produce gram quantities of fullerenes [4]; this technique reduced loss of carbon rods through complete heating of the electrodes. Figure 1.3 shows a typical arc process for fullerene soot generation. Two graphite rods are separated from each other by 1–10 mm in a helium-filled chamber under 100–200 torr pressure. An arc is discharged to generate 100–200 amp current at a voltage of 10–20 V. This process causes the graphite rods to evaporate and form soot containing fullerene products. Copper jacket covering the chamber wall and circulating cooling water control the temperature to allow carbon soot vapors to condense and deposit on the chamber walls, which can later be extracted for purification and processing. Modifications of these methods were performed to achieve several advantages. Such modifications include arc via contacting with the graphite [93, 214] or demineralized coal electrodes [186], employment of plasma discharge for high yield [189, 210], application of DC power rather than AC [93, 186, 214], and low current rather than high AC current [126], to achieve better fullerene yield, formation of tapered apparatus for gravity-based collection of carbon soot [126], etc.

Laser Ablation Method This technique was first adopted by the Smalley group in 1985 [136], which involves a laser, such as neodymium-doped yttrium aluminum garnet (Nd:YAG), irradiated on a graphite rod causing the carbons to evaporate via
heating and produce carbon plasma. Afterward, controlled cooling of the carbon plasma takes place to form fullerene clusters. Later, ablation at elevated temperature or inside of heated furnace resolved the issue by slowing down the cooling process [59, 147]. Around 1000–1200°C was found to be most efficient for fullerene cluster formation [147]. A high-temperature furnace containing such laser ablation arrangement is shown in Figure 1.4. Operating parameter modulation, such as changing laser intensity, wavelength, buffer gas pressure, and temperature in the furnace, can offer better control over fullerene formation and yield.

**Other Methods** Versatility in fullerene synthesis processes has been achieved through adoption of different innovative approaches. A thermal vaporization method by inductively heating the graphite rods in a high-frequency furnace at 2700°C was developed
for soot production at large quantities [190]. Moreover, combustion method was employed where laminar flames of premixed benzene and oxygen with argon diluents were used to produce C\textsubscript{60} and C\textsubscript{70} [102, 103]. Gram quantities of fullerenes were produced using this process with potential for easy scale-up, continuous process operations, easy dopant addition in the flame mixture, and changes in flame properties for controlling the fullerene size distribution [102, 147]. Efficient production of a large quantity of higher fullerene soot with minor C\textsubscript{60} presence was developed by Bunshah \textit{et al.} in 1992 [36]. Two different experimental setups were devised—one for carbon sputtering and the other for electron beam sputtering. In the carbon sputtering method, a magnetron sputtering cathode was attached to a graphite target, and carbon black was sputtered from the target by helium ions. In the other method, an electron beam was used to evaporate carbon from a graphite target. Efficiencies of fullerene synthesis methods along with their extraction methods, yields, and operating conditions, such as pressure, temperature, mode, etc., have been summarized in several review papers [188, 216].

1.3.1.2 Extraction, Separation, and Purification Fullerene extraction and purification involve a two-step process [63]. First, fullerene mixtures are isolated from the carbon soot using a solvent extraction, followed by a separation of individual fullerene molecules using chromatography or sublimation processes. Details of these processes are described in the following.

**Fullerene Mixture Extraction from Carbon Soot** In the solvent extraction method, fullerene mixtures along with some soluble hydrocarbons from the soot are dissolved in toluene or similar solvents and then filtered or decanted to remove the insoluble residue to recover extractable fullerenes at 10–44% mass [216]. Toluene-soluble extracts generally contain 65% C\textsubscript{60}, 30% C\textsubscript{70}, and 5% higher fullerenes [216]. Tetrahydrofuran (THF) is also used to ultrasonicate soot at room temperature, followed by filtration [58]. Evaporation of the filtrate in a rotary evaporator is employed to obtain fullerene powder mixture. A Soxhlet apparatus can also be used for efficient solubilization of fullerenes [63, 189]. In this process, the solvent is first boiled and evaporated, which is condensed down through a carbon soot matrix, extracting the fullerenes. The cycle is repeated for maximizing the fullerene extraction [189]. Sublimation process, in contrast, involves heating the raw soot in a quartz tube under helium gas or in vacuum followed by condensing the mixture [241]. Fullerene mixtures accumulate at the bottom, leaving the residue products from soot in the vapor phase.

**Separation and Purification of Individual Fullerenes from Mixture** There are two major processes for purification or isolation of individual fullerenes. These are solvent-based liquid chromatography (LC) and sublimation using temperature gradient.

**LC** This is the primary technique for separation of individual C\textsubscript{60}, C\textsubscript{70}, and other higher fullerenes from the extracted mixture [216]. In this process, a solution of fullerene mixture is passed through a packed porous column. The solution is known as the mobile phase, and the solvent as the eluent, while the solid surface is called the
stationary phase. Based on the molecular weight, fullerenes undergo chromatographic separation [251]. Selective separation of individual fullerenes with highest purity can be achieved by changing the stationary phase and eluent constituent and compositions [216]. Historically, a wide variety of mobile phases and stationary phases have been used for successful separation of fullerenes. The eluents include toluene [86], hexane [113, 181], toluene–hexane mixture [4, 230], pi-basic groups, etc. On the other hand, alumina [7], silica gel [4], graphite [240], C_{18} reverse phase [89], pi-acidic Pirkle phase [192], etc., have been reported to be used as developed stationary phases. The Soxhlet method has also been combined with the purification process to have a one-step extraction–purification technique for fullerene separation from raw soot [119]. This process loads fullerene mixture from top and separates individual structures employing a chromatographic column. Higher fullerene separation is achieved using high-pressure liquid chromatography (HPLC), which involves repeated and reversed chromatographic methods. The process utilizes solvents like carbon disulfide for achieving enhanced solubility of higher fullerenes. Gel-permeation-based chromatographic techniques have also been used for fullerene separations [163]. Commercially available HPLC systems have been found to use pyrenylpropyl and pentabromobenzyl groups as stationary phases for fullerene isolations [172]. Toluene and toluene–acetonitrile mixture have been found to be the most commonly used mobile phases for C_{60} and C_{70} separation, while chlorobenzene and dichlorobenzene are used for higher fullerenes.

**SUBLIMATION WITH TEMPERATURE GRADIENT** Differences in sublimation temperature and artificially created thermal gradient are used as the driving forces for the separation process [49, 260]. The raw soot containing fullerene mixture is directly added to a quartz tube under vacuum, and heat is applied at the center of the tube to raise the temperature to 900–1000°C. The tube containing the fullerene mixture has its one end at the center of the quartz tube, and the other is protruded outside of the tube in the ambient environment. Thereby, a temperature gradient is created from the center of the tube (hottest) to the outermost end. Individual fullerenes based on their sublimation temperatures deposit at different locations of the tube. Generally, higher fullerenes deposit closer to the center as they possess higher sublimation temperature compared to C_{60}s. Such spatial distance allows for purification of the individualized structures [22]. Several modifications have been performed on this method to improve separation efficiencies, which are elaborately described in other books and review articles [63].

**1.3.1.3 Chemical Synthesis Processes** Fullerene synthesis using chemical methods has been sought for obtaining a large quantity of isomerically pure fullerenes. However, only a couple of attempts have been successful developing such method, with only one that has realized into large-scale production so far [168]. Pyrolysis of naphthalene and its derivatives to obtain C_{60}s and C_{70}s through patching of C_{10} fragments encouraged researchers to adopt chemical pathways for fullerene synthesis [232]. Inspired by Barth and Lawton [138], Scott and coworkers presented their pioneering work of chemically synthesizing bowl-shaped corannulene
molecules (C\(_{20}\)H\(_{10}\)) using flash vacuum pyrolysis (FVP) process [209]. Later, the same group developed a rather ground-up chemical synthesis method where commercially available precursors, such as bromomethylbenzene and 2-naphthaldehyde, were used to form C\(_{60}\) [28]. Successive chemical reactions and modifications of these precursors lead to formation of polyarenes and their derivatives, such as C\(_{60}\)H\(_{30}\), C\(_{80}\)H\(_{40}\), and C\(_{60}\)H\(_{27}\)Cl\(_{3}\) [28, 208]. Finally, employing FVP at 1100°C can cause cyclo­dehydrogenation and cyclodehalogenation of these intermediates to produce notable quantities of isomerically pure C\(_{60}\) [28, 208]. However, the yield of this process is typically low (i.e., <0.4%), which restricts the use of this method for commercial production of fullerenes [207]. Newer techniques for fullerene fragment production and their conjugation processes have been proposed, which require further investigations and research to fully realize [168].

1.3.1.4 Fullerene-Based Nanohybrids Fullerenes can be hybridized with carbonaceous materials both endohedrally and exohedrally. Endohedral hybrid examples include nanopeapods [218] and nano-onions [219]. Fullerene molecules when entrapped within CNTs are called nanopeapods, while multilayered concentric fullerenes are known as carbon nano-onions. Such encapsulations are performed through thermal annealing [185, 218], carbon vapor deposition (CVD)-based growth processes [44], water-assisted electric arc [107, 185], or wet capillary filling processes [215]. Exohedral conjugations of fullerenes with CNTs [51] and graphene [194] require noncovalent functionalization; π–π interaction between functionalized mole­cules can hold the carbon allotropes together. However, covalent functionalization can also be performed. For example, porphyrin-derivatized fullerenes can provide bonding through amination reaction with the carboxy-functionalized CNTs [81]. Moreover, harsh chemical reactions forming seamless bonds can give rise to special form of hybrids named “nanobuds” [174, 255].

1.3.2 Characterization

With the advancement of nanotechnology, various techniques have been developed to characterize fullerenes and their hybrids [1–3, 201]. From production of soot to the formation of individual fullerenes, several characterization methods are employed to determine the composition, morphology, and concentration [63, 147]. Such tech­niques include mass spectroscopy, NMR, optical spectroscopy, HPLC, electron microscopy (EM), etc. We have limited our discussion to fullerene characterization only; NHs in the literature have mostly followed similar characterization tools. However, spectral, physical, and chemical signatures of NHs will differ significantly from fullerenes. This section will briefly describe key characterization techniques for fullerenes.

1.3.2.1 Mass Spectroscopy Mass spec has been one of the primary identification tools of the first fullerenes. Several mass spec methods have evolved over the years [188]. The key process in this characterization involves ionization and charged separation of neutral molecules according to their mass-to-charge (m/z) ratio. It is a
highly sensitive method that can detect as low as 10 ions, enabling detection of trace concentrations of fullerenes [35]. The ionization and desorption of molecules are generally done by laser-induced methods [38]. Other methods of ionization include thermal desorption [48], fast atomic bombardment [161, 189], electrospray ionization [98], etc. For detection of the ionized fullerene samples and their spectral recording, TOF [132] or Fourier transform mass spectrometry [63, 188] (FTMS) methods are used.

1.3.2.2 NMR NMR is also very useful in determination of fullerene and higher fullerene purity [121, 229–231]. 13C-NMR has been proven to bear the first evidences of fullerene structures, which led to the conclusion of C_{60}’s ability to follow the isolated pentagonal rule [132]. It is interesting to notice that the highest obtainable spherical symmetry of C_{60}, when produced or characterized in its purest form, presents with a singular peak around 142–143 ppm in the resonance spectra [147, 230]. On the other hand, five resonance peaks are obtained for the ellipsoidal shape of C_{70} fullerenes [115]. Stability of fullerenes in different reactive environments has also been understood employing NMR method [231].

1.3.2.3 Optical Spectroscopy The ability of light absorption by individual fullerenes differs based on the molecular weight and band structure of the fullerenes. While solubilized in toluene, C_{60} suspensions appear to be magenta or deep purple, whereas C_{70}s exhibit a color close to the red wine [63]. Other higher fullerenes show colors ranging from yellow to green with the increase in molecular weight of the fullerene molecules [68, 121]. Similarly, their light adsorption in infrared and UV region also differs that is utilized for spectral characterizations of fullerenes [147]. For example, Figure 1.5 shows UV–Vis spectral signatures of C_{60} and C_{70} aqueous suspensions. The suspensions were prepared by sonicating powdered fullerenes in a

FIGURE 1.5 UV–visible spectra of Pluronic modified C_{60} and C_{70} aqueous suspensions. (See insert for color representation of the figure.)
biocompatible polymer solution. UV peaks appeared at 275 and 350 nm for C\textsubscript{60}, while C\textsubscript{70} showed widening and broad shoulders at those wavelengths, lacking in distinct peaking behavior. C\textsubscript{70}s showed peaks close to 410 nm, consistent with the published literature [1, 2].

1.3.2.4 **HPLC**  HPLC is one of the key techniques for fullerene separation, as discussed earlier. Besides, HPLC can also serve as an effective analytical tool for purity assessment of C\textsubscript{60}s, C\textsubscript{70}s, and higher fullerenes [121, 147]. Moreover, HPLC can also be utilized for detection of fullerenes using the well-established elution times, proved to be reliable in the literature [147]. Such detection has been performed in commercial applications also. For example, in a 4.6 mm ID×250 mm standard commercial column, using toluene as mobile phase at 1.0 ml/min flow rate, UV peaks at 312 nm wavelength for C\textsubscript{60}, C\textsubscript{70}, C\textsubscript{76}, and C\textsubscript{84} fullerenes can be observed at 8, 12.5, 17, and 23 min, respectively, allowing for their individual characterizations [172].

1.3.2.5 **Electron Microscopy**  Since the evolution of scanning tunneling microscopy, fullerene structures were confirmed through visual observation [91]. Development of electron microscopic (EM) techniques over the years has allowed for detailed characterization of fullerenes during synthesis and during their postproduction application. EM techniques enable evaluation of size and morphological characteristics of molecular and clustered fullerenes. For example, Figure 1.6 shows high-resolution transmission electron micrographs (HRTEM) obtained for aqueous fullerene clusters, solubilized via sonication in polymeric aqueous suspension as mentioned earlier [1]. Figure 1.6a, b shows C\textsubscript{60} and C\textsubscript{70} clusters, respectively. Their morphology appears to be spherical. Figure 1.6c, d presents higher magnified images, confirming fullerene lattice fringes, proving the crystalline nature of the clusters.

1.3.2.6 **Static and Dynamic Light Scattering**  Fullerene clusters in suspension are characterized using light scattering techniques. Dynamic light scattering (DLS) and static light scattering (SLS) are the most popular tools that are employed to evaluate time-dependent cluster size, fractal dimension, and aggregation propensity of fullerenes and other nanomaterials [1, 2, 117, 118]. Such methods are particularly useful for environmental implication studies, where interaction of fullerene clusters in water under varying chemical conditions can be systematically studied [1, 43]. Here, we will discuss measurement of aggregation kinetics of C\textsubscript{60}s using DLS technique; detailed description of the SLS technique for determination of aggregate structure of carbonaceous nanomaterial is presented in a previous work by our group [118].

Time-dependent dynamic light scattering (TRDLS) intensity measurement can be performed on C\textsubscript{60} aqueous suspension against different environmentally relevant concentrations of NaCl salt. The C\textsubscript{60} aqueous suspension here was prepared by a well-established solvent exchange method [2]. An ALV/CGRS-3 compact goniometer system (ALV-Laser Vertriebsgesellschaft m-b.H., Langen/Hessen, Germany) equipped with 22 mW HeNe laser at 632 nm (equivalent to 800 mW laser at 532 nm) and high QE APD detector with photomultipliers of 1:25 sensitivity was used for this purpose. The obtained scattering data for each condition were used to profile
time-dependent aggregation of fullerene nanoparticles at each electrolyte condition as shown in Figure 1.7a. It is observed that with no salt addition and at low ionic concentration of NaCl (up to 10 mM), the hydrodynamic radius of C$_{60}$ clusters remained unchanged over time. However, increased aggregation is observed at higher salt concentrations. The initial slope of this profile is the initial rate of aggregation that is proportional to the initial rate constant ($k_i$) and also to the initial concentration of the fullerene suspension (Eq. 1.1) [202]:

$$k \propto \frac{1}{N_0} \left[ \frac{dR_n(t)}{dt} \right]_{t=0}$$  \hspace{1cm} (1.1)

Attachment efficiency ($\alpha$) of fullerene clusters at each solution condition can then be obtained through dividing the initial aggregation rate at each solution condition by the
initial aggregation rate at favorable condition for aggregation (which is obtained at high salt concentration). The theoretical formulation is expressed in Equation 1.2 [202]:

\[
\alpha = \frac{\left[ dR_n(t) / dt \right]_{t \to 0}}{\left[ dR_n(t) / dt \right]_{t \to t_{\text{fa}}}}
\]  

(1.2)

The attachment efficiencies can then be plotted against corresponding salt concentrations (Fig. 1.7b), known as stability plot. Figure 1.7b shows that C$_{60}$ aqueous suspension follows classical Derjaguin–Landau–Verwey–Overbeek (DLVO) behavior [43, 202]. Further, quantitation of the aggregation propensity of the fullerenes can be obtained by analyzing the stability plot.

**FIGURE 1.7** (a) Time-dependent aggregation profile of C$_{60}$ at different NaCl concentrations. (b) Stability plot for C$_{60}$ aqueous suspension at different NaCl concentrations.
1.4 ENERGY APPLICATIONS

A large number of fullerene-related publications offering insights into energy applications can be found in the literature. A recent literature search in Web of Science® has resulted in a total of 1626 publications from 1991 to 2012 that concern energy applications. The search was performed using a glossary of energy terms and a search algorithm designed with wild cards and Boolean operators. Title field tag and article-only document type were also combined in the search criteria to limit the obtained results. The literature search reveals that the energy application sector of fullerenes and related materials is at an early stage; however, there is a rather rapid increase in the fullerene energy application literature over the past decade (Fig. 1.8a). Most publications focus on fullerenes (89.2%), while less than 10% of the yearly publications are devoted to HOFs (0.3%), fullerene derivatives (6.1%), and/or hybrids (2.6%). The advantages of fullerenes and related materials on the energy application sector are derived from their fascinating characteristics: good acceptors of electrons and exceptionally low reorganization energies in electron transfer [7], superconductivity [94], absorption of light throughout the visible region [157], and their stability due to rigid spherical carbon framework [106].

The retrieved publications have also provided information regarding the various practical applications, which can be generally categorized as follows: (i) solar cells and photovoltaic materials, (ii) hydrogen storage materials, and (iii) electronic components. The technical literature also contains information on properties of fullerenes and related materials relevant to energy applications: (iv) superconductivity, electrical, and electronic properties and (v) photochemical, photophysical, and photocatalytic studies (Fig. 1.8b). The following section will briefly describe the different aspects and relevant properties of energy applications with fullerenes.

1.4.1 Solar Cells and Photovoltaic Materials

Some of the most promising applications for fullerene-related materials are solar cells and photovoltaic materials (~47% of the publications; Fig. 1.8b). The increased demand for low-cost renewable energy sources and the photoexcitation properties of C60s and related materials has generated interest for their application as novel photovoltaic materials and has motivated new approaches to production of efficient and inexpensive solar cells and photovoltaic devices.

Solar cells convert the energy of light into electricity by photovoltaic effect and consist of an electron donor and an acceptor material arranged in a bilayer structure of interpenetrating network. Organic materials, for example, conjugated polymers, have been explored as economic alternatives to inorganic semiconductors (silicon, amorphous silicon, gallium arsenide, selenide, etc.) currently used [266]. The discovery of photoinduced electron transfer from conjugated conducting polymers (as donors) and C60s (as acceptors) provided the first highly efficient plastic photovoltaic cell [77, 266]. C60-doped polymers, for example, polyvinylcarbazole (PVK), poly(paraphenylene vinylene) (PPV), and phenylmethylpolysilane (PMPS), have been reported to exhibit exceptionally good photoconductive properties [235, 246]. Organic photovoltaic materials of poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene]
Fullerene-Related Publications on Energy Applications

(a) Total number of publications on fullerene and related materials on energy topics. Note: Others correspond to HOFs, derivatives, and hybrids. (b) Energy applications of fullerenes, HOFs, hybrids, and its derivatives. Source: ISI Web of Science, September 2013.

FIGURE 1.8 (a) Total number of publications on fullerene and related materials on energy topics. Note: Others correspond to HOFs, derivatives, and hybrids. (b) Energy applications of fullerenes, HOFs, hybrids, and its derivatives. Source: ISI Web of Science, September 2013.
(MEH-PPV)/C$_{60}$ exhibit an enhancement in the photovoltaic effect with increasing C$_{60}$ concentration [122]. Several studies report the use of other C$_{60}$-doped polymer combinations for photovoltaic cells: methyl-ethyl-hydroxyl-polypropylvinyl (MEH-PPV)/C$_{60}$ thin film [204], poly(4-vinyl pyridinated) fullerenes (PVPyF) [137], ITO/polyalkylthiophene (PAT)/C$_{60}$/Al [182], and poly(3-alkylthiophenes)/C$_{60}$ [37]. However, material stability was found to be a persistent problem for applications of conjugated polymers that are simultaneously exposed to light and oxygen, causing rapid degradation of the materials [176]. Fullerene and high fullerene derivatives (e.g., oligophenylenevinylene (OPV) group attached to C$_{60}$ through a pyrrolidine ring [65], mono- and multiadducts of C$_{60}$ derivative PCBM and MDMO-PPV [75], PPV and PCBM [183], C$_{70}$/poly(2-methoxy-5-(3,7'-dimethyloctyloxy)-p-phenylenevinylene) (MDMO-PPV) [250], poly(2,7-(9-(2''-ethylhecy)-9-hexyl-fluorene)-alt-5,5-(4''7''-di-2-thienyl1',1',3'-benzothiadiazole)) (PFDTBT) and PCBM [222], C$_{70}$-PCBM [141]) have also been studied for incorporation in photovoltaic devices; however, such research is only in preliminary stages.

The use of hybrids for efficient solar energy conversion is also emerging. Studies have looked at chemically linked CdSe quantum dots (QDs) with thiol-functionalized C$_{60}$ hybrids. The photoinduced charge separation between CdSe QDs and C$_{60}$s opens up new design strategies for developing light harvesting assemblies [23]. Other studies have looked into the effects of incorporating CNTs in a polymer–fullerene blend host. Nanobuds (C$_{60}$-functionalized CNTs) were found to be disadvantageous and somewhat detrimental to overall photovoltaic device performance [8].

The use of fullerenes and other related materials has also been focused on enhancing the thermal stability of solar cells [217], improving the performance and efficiency of polymer–fullerene conjugates [154] and photovoltaic properties of new blends [112], and optimizing polymer–fullerene solar cells [120]. Driven by technology advances, a better understanding of fullerenes and their synthesis and processing techniques will likely allow to lower the cost of the material to meet the exponential demand of the energy industry [223].

1.4.2 Hydrogen Storage Materials

Hydrogen is a clean and renewable source of energy that could be generated by electrolysis of water. Only a small percentage of the publications surveyed here report on fullerene and related materials as storage devices for molecular hydrogen (~3%; Fig. 1.8b). However, it appears that fullerene and related materials may be promising toward storage capacities for hydrogen. In its gaseous form, hydrogen has a low specific volumetric energy density, compared to other liquid fuel sources. To increase its energy density, compressed hydrogen should be stored in a hydrogen storage material such as hydrogen storage alloys and CNTs [62]. Because of low efficiency from high frictional power loss, an electrochemical compressor using a membrane electrode assembly (MEA) film of proton (H$^+$) conductor is more effective than the conventional mechanical compressing methods [158]. However, humidity affects the proton conductivity and has to be removed from the compressed hydrogen. New fullerene composite membranes have been synthesized and have demonstrated enhanced
proton conductivity under low relative humidity conditions [187, 227, 243]. $C_{60}H_{36}$ has been under scrutiny as the source of hydrogen for the in situ hydrogenation of $(C_{59}N)_{2}$. It has led to $C_{59}NH_{5}$ as the main reaction product, identified by negative-ion mass spectrometry and providing evidence of the usage of $C_{60}$s as a storage device for hydrogen [239]. The electrochemical compression and hydrogen storage capacity using the MEA of fullerene-related materials (hydrogensulfated fullerenol) have been confirmed [158]. Studies also show that hydrogenation of carbon materials (fullerenes) requires activation centers [203, 239]. While considering these aspects, heteroatoms such as N, P, and S seem to be promising to behave as activators in heteroatom-containing carbon materials for hydrogen storage applications. Boron atoms have also been identified for low-energy hydrogenation [203].

It has been demonstrated that coated fullerenes are ideal for many practical hydrogen storage applications. A single Ni-coated fullerene can store up to three $H_{2}$ molecules (storage capacity up to 6.8 wt %) [213]. The capacity of charged fullerenes $C_{n}$ ($20 \leq n \leq 82$) as hydrogen storage media has been found to be up to 8.0 wt % [262]. Hydrogenated silicon fullerene has also been proposed for hydrogen storage with up to 9.48 wt % storage capacity [268]. Calcium has been proposed as a desirable metal coating to functionalize fullerenes and obtain high-capacity hydrogen storage materials with a hydrogen uptake up to 8.4 wt % [261]. Ti-decorated-doped silicon fullerene, Ca-coated boron fullerenes, and Mg-decorated boron fullerenes with storage capacities up to 5.23, 8.2, and 14.2 wt %, respectively, have also been reported [24, 143, 144].

1.4.3 Electronic Components (Batteries, Capacitors, and Open-Circuit Voltage Applications)

The incorporation of fullerene and related materials to improve the electrochemical performance of electronic components is scarcely reported by specific research groups, with publications in the last 10 years, dealing mostly with batteries [12–19, 193], capacitors [66, 116, 125, 253], and open-circuit voltage studies [50, 57, 79, 84, 129, 142, 166, 170, 177, 220, 236–238, 256, 267]. However, the demand of these components with higher capacity will likely increase to meet future demands.

1.4.4 Superconductivity, Electrical, and Electronic Properties Relevant to Energy Applications

Superconductivity is the event of exactly zero electrical resistance and expulsion of magnetic fields, occurring in certain materials when cooled below a critical temperature $T_{c}$ [92]. Zero resistance and magnetic field exclusion have a major impact on electric power transmission and also enable the development of much smaller electronic components that are more reliable, efficient, and environmentally benign for energy applications [85, 92]. Fullerene-based superconductors have drawn enormous scientific interest toward energy applications (~25% of the publications; Fig. 1.8b). In 1991, research on semiconducting technology found that alkali metal-doped films of $C_{60}$ lead to metallic behavior [88]. Shortly thereafter, these alkali-doped $C_{60}$s are found to be superconducting at $T_{c}$ that is only exceeded by the cuprates [70, 94, 101]. It was also
found that potassium-doped C\textsubscript{60} becomes superconducting at 18 K, making it the highest transition temperature for a molecular superconductor [94]. It has been discovered that the superconducting transition temperature in alkaline metal-doped fullerene increases with the unit-cell volume [275]. Cesium-doped fullerene (Cs\textsubscript{3}C\textsubscript{60}) has been reported to lead to superconductivity at 38 K under applied pressure in 1998 [76], but the highest superconducting transition temperature of 33 K at ambient pressure was reported for cesium–rubidium-doped fullerene (Cs\textsubscript{2}RbC\textsubscript{60}) in 1991 [225].

One of the biggest limitations of superconducting fullerenes is their instability in air; exposing the materials to air for a fraction of a second can completely compromise the superconductivity. Investigations in superconducting fullerenes continue as new combinations of surface and other fullerene-related materials are synthesized [27]. HOF analogues of the alkali-doped fullerenes have also been investigated; however, results indicate absence of superconductivity above 5 K [55]. A vast body of literature can be found on superconducting fullerenes and on the electrical and electronic properties of these materials. However, more research on superconductors using other fullerene-related materials is necessary.

1.4.5 Photochemical and Photophysical Properties Pertinent for Energy Applications

The photoactivity and the ability to “tune” fullerenes [40] and related material properties (i.e., band gap, chemical environment, conductance, thermal storage, etc.) are fundamentally important to fabricate devices for the collection, conversion, and storage of renewable energy (solar energy). Photochemical and photophysical properties of fullerenes and related materials result in the distinctive switching of chemical reactions, electrical energy, luminescence, degradation, absorption, and thermal and electrical properties of functional composites, which is crucial for novel devices with excellent performance.

In general terms, research in photochemical and photophysical properties of fullerenes revolves around optical absorption [82, 173, 191], photoluminescence and fluorescence [247, 265], excited state dynamics and properties of the singlet and triplet states [25, 72, 110, 152, 184], photochemical reactions [5, 6, 224], synthesis [21, 83, 105, 108], photocatalyst degradation [6, 134, 135, 165], singlet oxygen production, and charge transfer reactions [26, 30, 109, 178, 252, 264]. A fair number (24.2\%) of the retrieved publications deal with photochemical and photophysical information on fullerenes (Fig. 1.8b). However, additional progress is required given the diversity of fullerene and related materials and the necessity to functionalize and “tune” their properties for specific energy applications.

1.5 ENVIRONMENTAL CONSIDERATIONS FOR FULLERENE SYNTHESIS AND PROCESSING

Sustainable use of materials for energy applications not only demands for a renewable alternative with a small energy footprint but also necessitates low-risk involvement in the usage and disposal of such materials. Fullerenes, one of the most attractive
nanomaterials for energy applications, should present minimum environmental risk to be considered truly sustainable. However, fullerenes’ unique electronic properties are also known to be responsible for reactive oxygen species (ROS) generation, resulting in environmental toxicity. Moreover, synthesis and solubilization process of fullerenes and the soft polymeric and surfactant surface coatings (used for processing) will likely contribute to altered environmental risk. Thus, synthesis and processing of fullerenes, higher fullerenes, and their hybrids necessitate careful consideration for choosing potentially greener options [1, 3, 200, 201].

For example, organic photovoltaics, a major fullerene-based device, is an assemblage of multiple layers containing electron donors and acceptors, electrodes, and hole/electron transporters packaged within plastic materials such as poly(ethylene terephthalate) or PET [133]. These organic photovoltaics at the end of their usage will likely be disposed off to landfills [160, 175]. Though PET packagings are non-biodegradable, their fragmentation through abrasion and photodegradation under long-term exposure to sunlight are likely [69, 249]. Such degradation can lead to potential release of fullerene derivatives PCBM from the interior of these solar cells [277]. During their residence in landfills and the material exposure to soil surfaces and water (after being carried via surface runoffs), these fullerene, their derivatives, and associated solvents will inevitably interact with the aquatic environment and terrestrial ecosystems. Thus, true sustainable energy generation requires a thorough understanding of material energy cost as well as environmental risks associated with environmental fate, transport, and exposure.

### 1.5.1 Existing Environmental Literature for C_{60}

C_{60} and its several derivatives, including PCBM, have been systematically studied to better understand their fate and transport, environmental transformations, and toxicity toward aquatic species. It is important to note here that fullerene preparation methods and the chemical identity of the surface moieties of their derivatives can play a significant role in their environmental behavior. Fullerene cluster size and surface chemistry are known to impact their environmental behavior [43, 150, 248]. Importantly, the initial cluster size and surface chemistry are found to differ based on fullerene processing techniques; while extended mixing of water results in larger fullerene clusters with rough irregular edges, solvent exchange using toluene or THF as intermediate can produce smooth round edge crystalline structures [33]. Similarly, surface charge of the aqueous suspension using THF as intermediate was found to be significantly more negative compared to that produced via extended mixing [32]. Systematic evaluation of aqueous C_{60} and their derivatives showed such technique-dependent behavior; the OPV-containing PCBM and corresponding butyl (PCBB) and octyl (PCBO) esters showed exceptionally high stability compared to pristine aqueous C_{60} [29]. Mobility of fullerenes in porous media and their interfacial interaction are also highly dependent on the preparation methods [41], stabilizing agents [248], and particle size [41]. For example, toluene-dissolved aqueous C_{60} was found to show higher toxicity to Japanese medaka fish compared to C_{60}s solubilized with dimethyl sulfoxide (DMSO) any extended stirring [123]. Toluene-dissolved C_{60}
suspension exhibited spherical aggregates, while the other methods formed mesoscale aggregates. Thus, synthesis and preparation techniques of fullerenes can allow for environmentally friendly alternatives.

C\textsubscript{60} aqueous suspensions are known to show toxicity to microbial entities in aquatic [73, 150] and soil [114] media, other invertebrates [180], and fish [180]. There have been evidences of genotoxicity [56] and developmental toxicity [226] induced by C\textsubscript{60} aqueous suspensions. Several mechanisms for fullerene toxicity are postulated that include ROS-mediated oxidative damage [205], lipid peroxidation of cell organelles [206], direct contact with the cell membrane, and consequent membrane protein oxidation. Such toxic potential depends on the physicochemical characteristics such as surface charge and aggregate sizes [41, 150] as well as on preparation methods [73, 150] or solvents used [150]. For example, continuous sonication and separation through filtration of fullerene suspensions yield smaller aggregates that tend to produce more ROS leading to increased antibacterial effects [41]. Solvent effects on C\textsubscript{60} toxicity evaluations, on the other hand, have created controversies in the literature [96, 97]. Toluene- and THF-based fullerene suspensions have shown significantly higher toxicity compared to solvent-free ones [96, 97, 276]. In some cases residual toluene or THF and their degradation by-products were also found to be more responsible for the enhanced toxicity than the pristine C\textsubscript{60} aqueous suspension [96, 97]. It is also important to note that fullerene and its derivatives are often coated with polymers or surfactants to attain desired properties. Many of such synthetic molecules possess either nonbiodegradable polyaromatics or cyclic organic compounds. Such moieties have already reported to exhibit toxic behavior. For example, gamma-cyclodextrin–C\textsubscript{60} aqueous suspension showed higher photodynamic activity under UV illumination than polyvinyl pyrollidone (PVP)-dissolved C\textsubscript{60} [67]. Similarly, Tween-80 induced higher toxicity to \textit{E. coli} when compared to \textit{N,N}-dimethylformamide in solubilizing C\textsubscript{60} [47]. Thus, not only solvents used for fullerene synthesis but also chemical moieties used to functionalize these carbon allotrope surfaces need careful evaluation to reduce environmental risk. However, it has been found that the solvents’ inherent toxicity is increased when it is associated with fullerenes [52].

Environmental transformation of C\textsubscript{60}s through reaction with atmospheric oxygen [234] or ozone or via photochemical reactions under sunlight or UV irradiation or by adsorption of bio- and geomacromolecules (e.g., humic and fulvic acids) is also inevitable. Such transformations, which are likely going to be influenced by their synthesis and processing techniques, will also influence their subsequent environmental interactions. Sunlight or UV exposure to fullerenes is inevitable in the natural environment, which is known to cause chemical transformation of fullerenes by surface alteration via oxidation [139]. Such functionalization can enhance their stability in water, thus making them more persistent [145] in aqueous environment. Similarly, dissolved organic matter (NOM), generated from degradation of flora and fauna, can coat fullerene surfaces and stabilize their colloidal presence in water [271]. Dissolved organic matter in wastewater effluent was also found to inhibit fullerene aggregation by providing similar steric stabilization [258]. Thus, alteration of fullerene interaction in water can occur as a result of a combined presence of
sunlight and NOMs [195]; where sunlight-induced functionalization can inhibit humic adsorption of fullerenes [195], humics can reduce UV-inflicted oxidation via scavenging of ROS [104]. Transformations of C_{60} by ozonation or UV irradiation have shown to increase ROS production and subsequent E. coli inactivation [45, 46]. NOMs when interacting with fullerene suspensions can affect the triplet excited state, an intermediate state responsible for ROS generation [127]. While NOMs can quench such photoactivity of pristine C_{60} suspensions, they can enhance it for fullereneols [127]. Therefore, a complex interplay of both NOM and sunlight exposure will determine the environmental fate of the fullerenes and necessitate systematic evaluation.

### 1.5.2 Environmental Literature Status for Higher Fullerenes and NHs

Unlike C_{60}s, environmental considerations of higher fullerenes (e.g., C_{70}, C_{76}, C_{78}, C_{84}, C_{90}, etc.) and NHs have mostly been ignored [2, 3, 200, 201]. A limited number of studies evaluated colloidal properties [2, 53, 153] and toxicity [211] of C_{70}s. One of the previous studies from the authors’ group incorporated additional higher-order fullerene (i.e., C_{76} and C_{84}) colloidal property evaluations upon aqueous solubilization [2]. These studies show that higher fullerene hydrodynamic radii and surface potential differ substantially from those of C_{60}s. The enhanced surface potential measured in higher fullerene suspensions appeared to have originated from differences in their molecular structures and their enhanced electronegativity [199]. It is probable that such differences in electronic properties will alter their interfacial interaction in the environment; predicting such behavior of these higher fullerenes from C_{60}s is thus unrealistic. It is likely that stabilization achieved via increased electron density will make the higher fullerenes more mobile in the aqueous media. Our unpublished work with four different fullerenes (C_{60}, C_{70}, C_{76}, and C_{84}) shows evidence of such behavior.

Toxicity studies on D. magna, an aquatic organism, showed acute toxicity in presence of gallic acid stabilized C_{70} suspensions; mechanism identified was oxidative stress generated from fullerenes [211]. It is also to be noted that higher fullerene isomers possess smaller band gap, which can make them more reactive [61] compared to C_{60}s and C_{70}s, influencing ROS generation and subsequent toxic potential of the materials. Such band gap-modulated toxicity mechanism is already demonstrated in the case of metal nanoparticles [269]. NHs, on the other hand, have not yet been studied for environmental fate or toxicological implications. However, it can be safely argued that fullerene, their derivatives, and higher fullerenes when conjugated to form NH ensembles will likely present altered electron charge transfer, band gap, photoactivity, sorption properties, morphology, etc., which will result in a unique environmental behavior. The state-of-the-art literature shows a major gap in knowledge for risk and safety evaluation of higher fullerenes and fullerene-based NHs [2, 3, 200, 201].

### 1.5.3 Environmental Considerations

Based on the existing literature, it is clearly evident that advantages of fullerenes do not come without associated environmental risk. Figure 1.9 presents a schematic showing probable release of fullerene and its homologues from energy applications
to the environment as well as their fate, transport, and transformation, leading to potential environmental risk. Therefore, choice of synthesis and processing techniques as well as chemical functionalization of fullerenes should be considered keeping environmental risk factors in mind. $C_{60}$s, higher fullerenes, and NHs will
likely to be, if not already, used in commercial energy applications. Exposure of these materials during manufacture, use, or end of life is thus likely and should be considered for their design and production. This section discusses key considerations of fullerene use in energy applications and identifies some relevant aspects critical to ensure environmental safety.

1.5.3.1 Consideration for Solvents Solvents used to formulate the electron donor/acceptor (P3HT:PCBM) blends or thin films generally consist of chlorobenzene [124, 171], dichlorobenzene [124, 171], orthoxylene [171], mixture of chloro- and nitrobenzene [171], chloroform [167], and toluene [274] (Fig. 1.10). Most of these solvents possess aromatic groups and are halogenated, which are known as nonbiodegradable as well as toxic [64]. Thus, choosing these solvents may compromise environmental safety due to the residual in the solar cells. Similarly, solvents used for fullerene processing, for example, aqueous solubilization, may also pose such risks; for example, THF or toluene. For greener synthesis of energy devices, comparatively benign, short-chain substituted alkanes (e.g., chloroform) can be opted [64]; or novel solvent-free methods for blend formation can also be developed [39]. Thermal annealing process for morphological control of the P3HT:PCBM film can be chosen over solvent evaporation annealing to reduce solvent use. However, such alternative decisions require systematic studies comparing solvent effects with energy efficiencies of synthesized and/or processed fullerenes.

1.5.3.2 Considerations for Derivatization Fullerene derivatives, for example, PCBM, can have $C_{60}$ and $C_{70}$ as origins, which are mostly employed as the electron acceptors [31]. Recently, higher fullerenes, that is, $C_{84}$-based PCBM derivatives, have also been studied for solar cell applications [128]. Methanofullerenes like...
PCBM have shown toxic effects to *D. magna* [34], which can be reduced through substitution with low toxicity derivatives. Substitutions of phenyl group with thienyl groups and other alkyl analogues can also present lower-risk alternatives. Other fullerene derivatives used should also be carefully considered, since many of such possess aromatic rings and/or cyclic chemical structures with less biodegradability. For example, indene fullerene [273], 1,4-di(organo)fullerenes [159], dihydronaphthyl fullerenes [54], penta(organo)fullerenes [179], etc. contain such nondegradable chemical structures, whereas fulleropyrrolidines [10] can be more bio-friendly. Moreover, derivatization is also performed using certain chromophores to enhance photoinduced charge transfers, such as porphyrin, phthalocyanines, etc. [254]. Such chromophores with potential safe usage for fullerene derivatization should be carefully evaluated for their biodegradability.

1.5.3.3 Consideration for Coatings Moreover, fullerene processing involves use of polymers or surfactants to enhance their dispersion as well as photophysical properties. However, it has been determined in studies that biocompatibility and aggregation behavior depend significantly on the coating characteristics on fullerenes or other nanomaterials [233]. For example, fullerene suspensions stabilized with sodium dodecyl sulfate (SDS) and Triton X 100 produced higher ROS compared to pure fullerene water suspensions [140]. Furthermore, transformation processes in the environment can become complex as overcoating of these coated fullerenes with geo- and biomacromolecules will alter their environmental persistence as well as potential risk [60].

Fullerene synthesis, processing, and separation thus require an underlying risk consideration. Properties of the solvents used, relative degradability of the derivatives and coatings, contribution of coatings on environmental safety, and such similar issues should be considered for safer usage of fullerenes in energy applications. A few critical questions that should be asked to pursue lower risk in fullerene’s energy applications are listed below:

1. Are the solvents chosen for fullerene synthesis and separation relatively less toxic?
2. Are there environmentally safer alternatives while derivatizing or hybridizing fullerenes?
3. Are the chemical moieties used to coat fullerene surfaces environmentally benign?
4. Can the fullerenes be immobilized to reduce their release from the devices or processes?

However, environmental considerations should pose these questions at a minimum, encouraging a more systematic and complete environmental study. Effective and sustainable use of fullerenes in energy applications requires attaining environmentally safe usage of these materials, which has been a missing link in most material science research and development.
REFERENCES


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