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Incorporation of Balls, Tubes, and Bowls in Nanotechnology

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Abstract The development of nanotechnology has been spearheaded by the development and discovery of new materials. The earliest materials theorized to be used in nanotechnology were fullerenes and nanotubes. Although fullerenes and nanotubes have a rich history in the area of nanotechnology, fullerene fragments, which share some the same properties as fullerenes and nanotubes, show potential in the field of nanotechnology as well. Fullerene fragments were synthesized close to 20 years prior to the discovery of fullerenes; however due to their complex synthesis they remained in relative obscurity in the field of nanotechnology. More recently, improved syntheses of corannulene and other fullerene fragments on an industrial scale have led to their potential in industrial applications. With the mass production of corannulene finally being realized, many new structures and exciting properties are making its way into the chemical literature.

Keywords Corannulene · Light Emitting diodes · Nanotechnology

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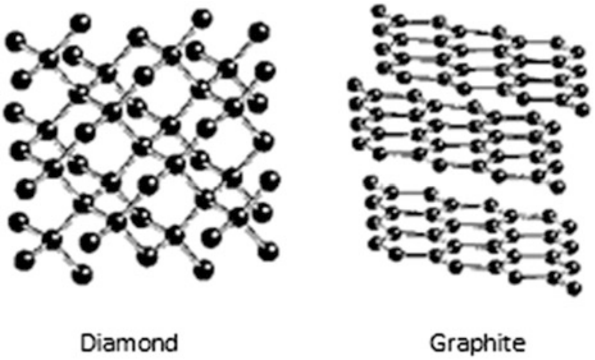


Fig. 1 Structures of a diamond lattice and graphite

1 Nanotechnology

Nanotechnology is a broad term that encompasses a wide range of topics within the scientific world. The idea of nanotechnology was conceived by physicist Richard Feynman at an American Physical Society meeting in 1959 with the idea that you could manipulate one set of atoms or molecules in order to build and control another proportionally smaller set of atoms or molecules [1]. The term nanotechnology was first coined by Professor Norio Taniguchi in a 1974 conference, describing it as “the processing of, separation, consolidation, and deformation of materials by one atom or one molecule.” In 1981 the invention of instruments such as the scanning tunneling microscope helped to move the concept of nanotechnology forward [2]. Shortly thereafter fullerenes and nanotubes were discovered, thus bringing carbon into the exciting world of nanotechnology. Carbon is the 15th most abundant element in the Earth’s crust, and the 4th most abundant element in the universe; considerable quantities occur in organic deposits of coal, oil, and gas and are the chemical basis of all known life. Until the twentieth century only two allotropes of carbon were known – diamond and graphite. Although both are forms of carbon, their physical properties differ greatly. Carbon atoms in diamonds are arranged in a face-centered cubic crystal structure called a diamond lattice and have strong covalent bonds between them, leading to the highest hardness and thermal conductivity of any bulk material. Diamond is also vastly transparent and is known for its unique optical properties. Graphite on the other hand has a layered, planar structure and its unique electrical conductivity is due to the high aromaticity leading to considerable electron delocalization between the carbon layers (Fig. 1). Graphite is the most stable form of carbon and is an excellent electrical conductor. Graphite is black in color and is most commonly used as “lead” in pencils and as lubricants.

Buckminsterfullerene (C_{60}) is a relatively new allotropic form of elemental carbon and is produced during the studies of nucleation in a carbon plasma formed by laser evaporation of graphite [3]. Buckminsterfullerene (C_{60}) was named after Richard Buckminster Fuller, a noted architectural modeler who popularized the geodesic dome. Fullerenes or “buckyballs” exhibits a closed carbon framework

Fig. 2 Structural relationship of fullerene (C_{60}) and an American soccer ball

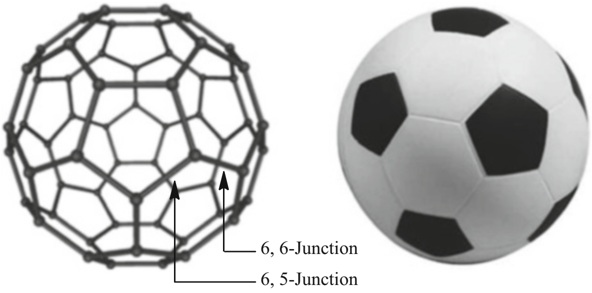
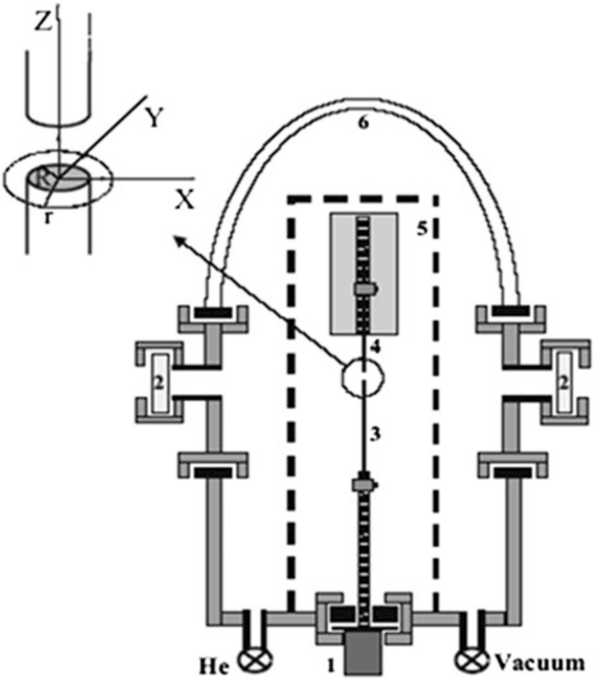
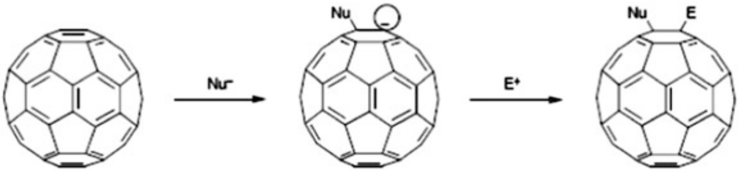


Fig. 3 Graphite electrode arc chamber: (*1*) motor for anode position control to maintain a constant inter-electrode distance, (*2*) quartz optical access ports for plasma spectroscopy, (*3*) anode, (*4*) cathode, (*5*) electrode holding platform, (*6*) glass dumbbell



with 20 hexagons and 12 pentagons (Fig. 2) and resembles an American soccer ball. Fullerene carbon atoms are sp^2 hybridized and form geodesic cages.

The C_{60} molecule has two different bond lengths. C–C bonds at 6–6 junctions (between two hexagons) can be considered as double bonds and measure 1.40 Å, whereas C–C bonds at 6–5 junctions (between a hexagon and a pentagon) are longer and measure 1.45 Å [4]. Although C_{60} is the most stable and abundant fullerene, higher fullerenes (i.e., C_{70}, C_{76}, C_{84}) are found as small impurities. In 1990 Kratschmer and Huffman developed a way to synthesize gram quantities of fullerenes by passing a current between two graphite electrodes in an atmosphere of helium, causing the graphite to vaporize (Fig. 3) [5]. At present, C_{60} is manufactured on a metric ton scale every year.



Scheme 1 Generic schematic of nucleophilic attack of C_{60} followed by quenching by electrophile

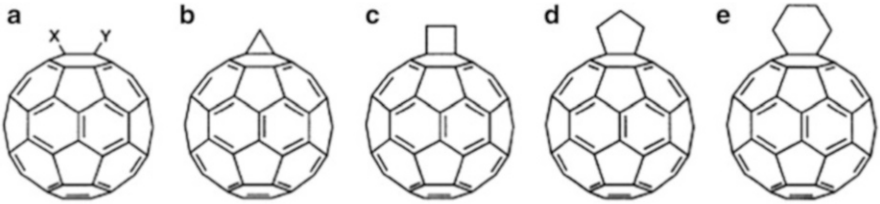


Fig. 4 Geometrical shapes of built onto a 6–6 ring junction of C_{60} (a) 1, 2 addition, (b) cyclopropanation, (c) 2+2 addition, (d) 3+2 addition, (e) 4+2 addition

Unlike diamond and graphite, fullerenes (C_{60}) are chemical reactive, having the chemical reactivity similar to that of an electron deficient olefin. C_{60} reacts readily with nucleophiles and is a reactive component in cycloadditions. The majority of reactants attack the 6–6 ring junctions of C_{60}, which possess more electron density. The insertions into 5–6 ring junctions have been reported only as rearrangements following a 6–6 junction attack. Adducts of C_{60} can be achieved by addition of a nucleophile followed by quenching with an acid or an electrophile (Scheme 1). Usually a 1,2-addition is observed, with many different adducts possible (Fig. 4).

Since their first detection and bulk production, fullerenes have played a leading role in the development of nanotechnology. Fullerenes are of great interest in this emerging field because they possess unique structural and electrical properties. The unique properties of fullerenes are desirable for various fields including nanoelectronics and materials science [6]. Fullerenes have numerous applications which include incorporation into polymers to obtain electroactive polymers or polymers with optical limiting properties, incorporation into thin films, and the design of novel molecular electronic devices. Furthermore, fullerenes have also been selected for potential uses in medicine including enzyme inhibition, photodynamic therapy, and electron transfer [7]. Its unusual closed geodesic structure can also be used for the entrapment of molecules.

2 Nanotubes

Carbon nanotubes are allotropes of carbon that were originally discovered in 1991 by Sumio Iijima [8]. Several techniques have been developed to produce nanotubes in large quantities, including arc discharge. Nanotubes were first observed in the

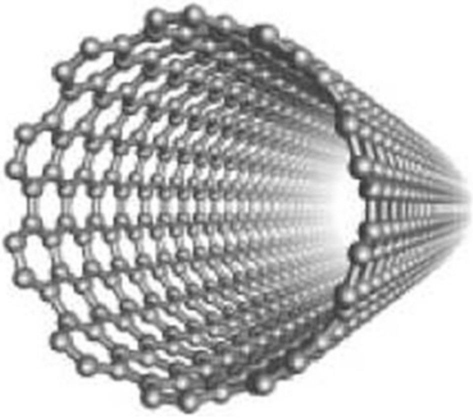


Fig. 5 Single-walled nanotube (SWNT)

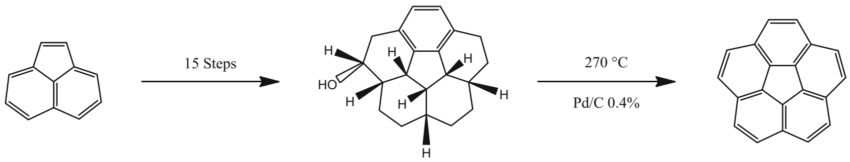
carbon soot of graphite electrodes in an attempt to produce fullerenes, similar to the method used by Kratschmer and Huffman. This method is the most widely used to produce nanotubes with yields of up to 30% [9].

Nanotubes can be classified as "cylindrical fullerenes" and are usually only a few nanometers wide. Nanotubes can be classified as single-walled nanotubes (SWNTs) or multi-walled nanotubes (MWNTs) (Fig. 5).

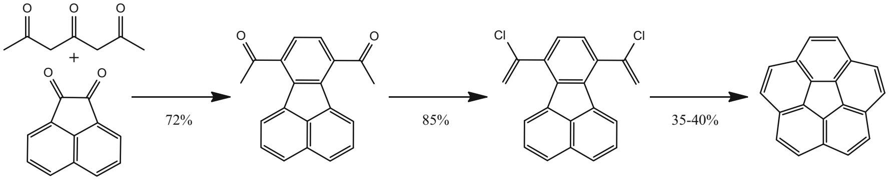
Since nanotubes are in the same class of molecules as fullerenes, they possess similar properties and applications. Nanotubes have properties that include high tensile strength, high electrical conductivity, high ductility, high resistance to heat, and relative chemical inactivity. Although fullerenes and nanotubes have the above-mentioned unique structural and physical properties, current methods in which they are synthesized make it difficult to modify them chemically for specific tasks. Since their discovery, there have been thousands of publications and patents exploring their unique properties; however, progress towards tailoring them for specific chemical tasks has been slow [10, 11]. The "difficult processability" of fullerenes and complex mixtures prove troublesome for specific applications. Furthermore, the inability to reproduce single walled nanotubes consistently is still a major concern. It is these issues that limit the implementation of these molecules into viable uses in nanotechnology.

3 Corannulene

The advancement of nanotechnology is reliant on the discovery of new and promising materials. The area of fullerene fragments has been around for nearly 40 years, but has mostly been overlooked in the field of nanotechnology due to the original lengthy synthesis and small quantities produced. Corannulene, which represents one third of C_{60}, consists of a cyclopentane ring fused with five benzene rings. Corannulene was first synthesized in the 1960s by Barth and Lawton. The



Scheme 2 Barth and Lawton's multi-step synthesis of corannulene (1)



Scheme 3 Flash vacuum pyrolysis of corannulene

original synthesis was long and cumbersome with an overall yield of only 0.4% (Scheme 2) [12, 13].

Barth and Lawton were able to determine a bowl shaped geometry for corannulene, resulting in unusual strain associated with the central five-member ring. Furthermore, they concluded that all ten hydrogens on the outer rim of corannulene were equivalent, resulting in a singlet in the ^{1}H NMR spectrum.

Corannulene research went nearly dormant for over 2 decades. The original 17-step synthesis hindered any further insight into the chemical behavior of the novel hydrocarbon. The discovery of fullerenes and nanotubes renewed interest in this unique molecule. In the early 1990s, Scott (Scheme 3), Siegel, Rabideau and others proposed much shorter higher yielding syntheses of corannulene, making this unique molecule more available [14–19].

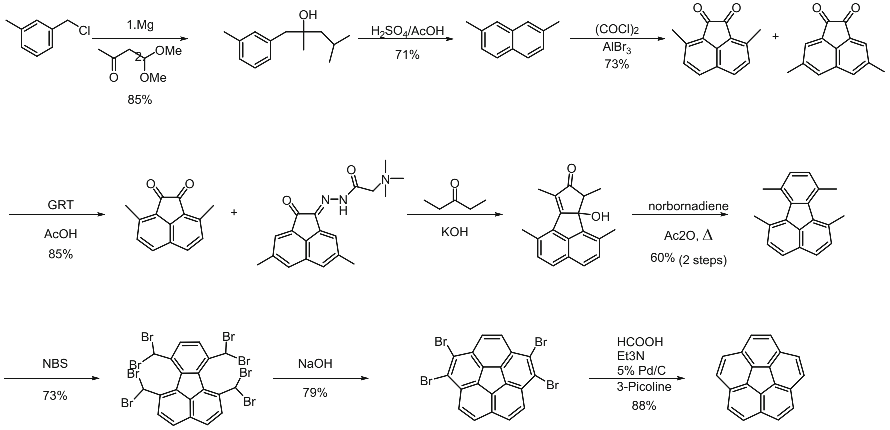
Although corannulene could be produced in larger quantities it was still far behind the commercialization of fullerenes and nanotubes. Therefore it was integral that a solution-based model be developed in order to obtain large scale quantities.

It is of great importance that macroscale quantities of corannulene be produced in order for its unique properties to be fully explored, leading to its implementation into the field of nanotechnology. Recently Siegel and co-workers have demonstrated the ability to produce kilogram quantities of corannulene (Scheme 4) [20].

Corannulene is of great interest because it has similar properties to that of fullerenes and nanotubes. Corannulene's structure is similar to C_{60} in that it maps perfectly onto its surface, as shown in Fig. 6.

Corannulene is one of only a few hydrocarbons to have a strong dipole moment, which is 2.07 D [21]. In comparison, water has a dipole moment of 1.8 D and ammonia that of 1.5 D. It also has a curved structure with its electron density localized in the center of the bowl, shown here in Fig. 7.

Furthermore, corannulene is one of only a few organic molecules to possess electrochromic properties. Electrochromism refers to the reversible color change



Scheme 4 Large scale synthesis of corannulene synthesis of corannulene

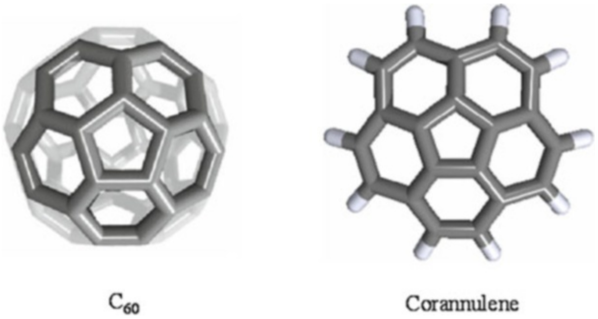


Fig. 6 Structural relationship between C_{60} and corannulene

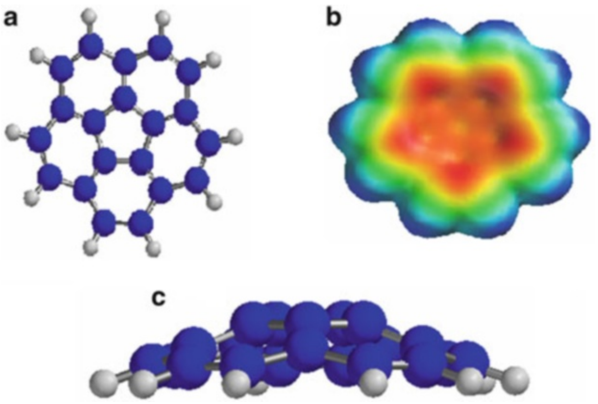


Fig. 7 (**a**) Molecular structure of corannulene. (**b**) Electron-density of corannulene. (**c**) Curvature of corannulene

associated with a chemical or electrochemical reduction. C_{60} has a triply degenerate low lying LUMO and has been shown to be electrochemically reduced six times, with reduction potentials of −0.98, −1.37, −1.87, −2.35, −2.85, and −3.26 eV [22–24]. Similarly, corannulene has a doubly degenerate low lying LUMO that can accept up to four extra electrons. In 1967, the first two reductions of corannulene were discovered and reported to be 1.88 and 2.36 eV [25]. Additionally, noticeable color changes associated with each reduction were observed. The first reduction gives a green color and the second reduction is associated with a bright red species. Attempts at this point to obtain a third and fourth reduction were unsuccessful. It was also noticed that the oxidations produced a polymeric product that blocked further oxidation. The third and fourth reductions were achieved later using lithium wire [26]. The third reduction gave a color change to purple, while the fourth reduction gave a brownish color. To date, the electrochemical reduction potentials of the third and fourth reductions are absent from the literature since the experiments were done using NMR. One field in which the electrochromic nature of coannulene would show great promise is in the area of organic electronics.

Organic electronics have been of interest in several fields such as chemistry and physics for more than 50 years [27]. Until recently, the electronic and optical phenomenon of these materials was restricted to academic research because of their limited practical applications. For example, electroluminescence from anthracene crystals manifested in 1960 by Pope et al. disclosed the phenomenon of organic electroluminescence [28]. Unfortunately, the application of organic light emitting diodes (OLEDs) was still unrealistic due to high operating voltage and catastrophic decay of light in just few minutes of operation [29, 30]. However, the ability of synthetic chemists to modify the chemical structure in ways that directly impact the properties of the materials when deposited in thin film form has provided a new direction to this field. A breakthrough was made by Tang et al. and Slyke at Kodak, who demonstrated the use of a low voltage and highly efficient thin film light emitting diode [31]. Their double-layer design soon became a landmark achievement and a prototypical structure in OLEDs. Even though results reported were not on par with existing technology, their discovery opened the door for the possible use of organic thin films based on light emitting diodes (OLED) as a platform for future generations to come. In the last 15 years the field of organic semiconductors has transformed itself rapidly from a topic of academic research interest to a wide range of applications, which include polymers LEDs [32], small molecule-based OLEDs [33, 34], organic lasers [35], organic transistors [36], and solar cells [37]. The commercial success of OLEDs is driven purely because of their low production cost, flexibility, and lower power consumption. However, key issues like control over desired emission colors with high emission intensity, efficiency, and the ability to display both electrical and optical stability for longer periods of time remain a bottleneck for today's synthetic chemists in designing these materials. More importantly, the synthesis of stable blue electroluminescent organic molecules with high efficiency and good color purity at practical levels of brightness remains a challenge [38].

Although the OLEDs have come a long way there are still major hurdles which must be addressed in order to advance the field further. A major concern that plagues OLED display is their shorter lifetimes, especially for blue OLED materials [27, 38]; typical lifetimes are 46,000–230,000 h in the case of red and green OLEDs but only 14,000 h for blue OLEDs. As OLED devices display pictures with high brightness, such a phenomenon would lead to higher voltages across a larger band gap, especially for blue emitting materials in comparison to their green and red counterparts, and hence, would result in faster degradation of blue emitting materials compared to green and red. Another issue is uneven color balance; over the period of time OLED material which produces a blue color tends to degrade faster than the rest, resulting in poor picture quality with unnatural color saturations.

Hence the future and thereby market capitalization of OLED-based display technology relies greatly on synthesizing more robust, thermally stable, easily processed and high quantum yield blue emitting OLEDs. Typically carbon is a poor conductor of electricity; however, carbon-based systems could act as good conductors when arranged in the form of a conjugated π system. Conduction of electricity followed by its electroluminescence properties are based on band gaps, ionization potentials, and the differences between energies of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The difference between these two MOs is known as the HOMO–LUMO energy gap and is related to the minimum energy needed to excite an electron in a molecule. The energy required for an electronic transition corresponds to the molecules' wavelength of radiation. An alkene bond is described by two π orbitals of different energies, bonding and antibonding. In a conjugated molecule there is an effective overlap of π orbitals, resulting in a π–π conjugated system. Each additional alkene bond extending conjugation creates two new energy levels allowing the HOMO-LUMO gap to lessen. The decreased gap requires less energy to excite an electron and bathochromically (red shift) shifts the wavelength of emission possibly into the visible region; hence it is a vital tool to control and fine tune emission color.

Looking at the band gap comparison of polyenes, acenes, fullerenes, and corrannulene, we observe drawbacks for the use of aromatics in OLED fields (Fig. 8) [39].

Let us take a moment to examine various carbon-based conjugated system with reference to their band gap, commercial availability, and processability issues.

Initially, poly(*p*-phenylene-vinylene) (PPV) was used as an active material in fabrication of an OLED (Fig. 9) [40]. PPV is insoluble and difficult to process, and its incorporation into an OLED was via a soluble precursor method. This technique often involved intensive labor hours and generated high cost.

In an attempt to improve processability, PPV derivatives bearing long alkyl chains [41], alkoxy substituents [41, 42], and even metals [43, 44] were introduced following classical synthetic organic methods. However, steric repulsions between side chains cause a marked twisting of polymer backbones leading to very short conjugation lengths and corresponding aggregation leading to a shift of emission into UV region. Additionally, conjugated polymeric materials are difficult to

Fig. 8 Band-gap comparison of different π-conjugated system

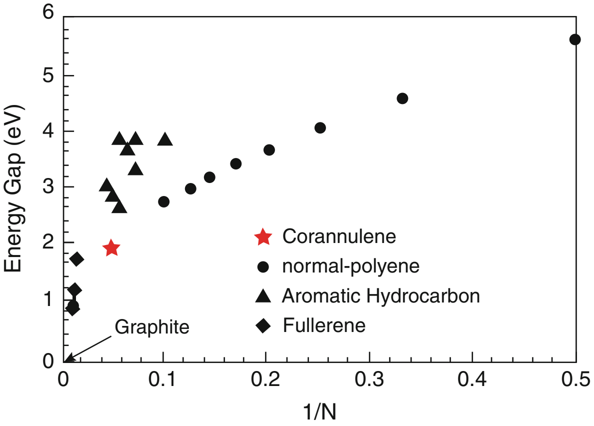
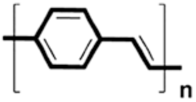


Fig. 9 Poly(*p*-phenylene vinylene)



synthesize and purify. Once an impurity is built in, it can either be removed by chemical treatment or thermal conversion.

Next in the series are cyclic conjugated acenes: anthracene, tetracene, pentacene, hexacene, etc. With increasing numbers of benzenoid rings, the band gap rapidly decreases and so does chemical stability. For example, both green-hexacene and violet-pentacene must be handled under an inert atmosphere. Similarly, dark-green heptacene has never been obtained in a pure state due to rapid oxidation in air [45]. Moreover, strong π–π interactions are responsible for their aggregation in solution phase, thereby raising concerns over their processing to produce thin films. To help improve processability in the case of anthracene, bulky substituents were introduced at the 9, 10- positions [46, 47]. Substituents introduce steric strain to help limit intermolecular π–π interactions and enhance solubility. Literature proceedings also suggest that anthracene derivative-based devices showed recrystallization during device operation because of high voltage, leading to device failure [48].

Fullerenes also show photophysical properties but these properties are not easily modified. They absorb strongly in the ultra-violet region of the electromagnetic spectrum, with slight trailing into the visible region, as depicted in Fig. 10 [49]. However, attempts to lower band gap by connecting two fullerene units together with an acetylene bridge introduce an sp^3 hybridized carbon which disrupts the overall conjugation. Hence, even though two fullerenes are connected, because of disruption in π-communication each fullerene unit acts independently from each other. As a result there is no net reduction of band gap.

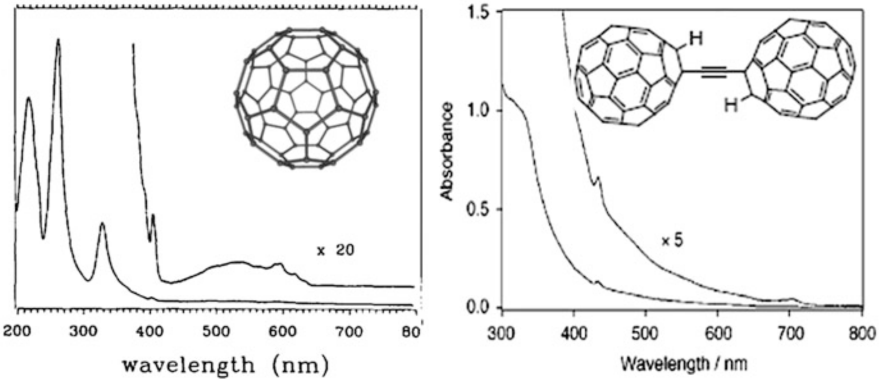


Fig. 10 UV-vis spectra of fullerene and difullerenylacetylene

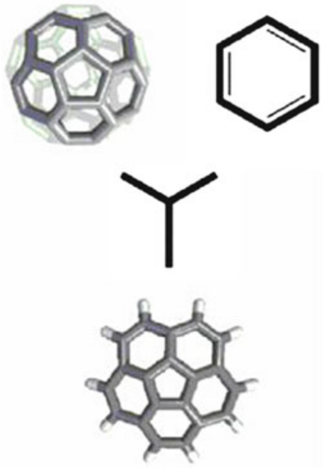


Fig. 11 Structural and chemical similarities of (**1**) with fullerene [C_{60}] and benzene

Carbon nanotubes are allotropes of carbon rolled into the form of cylindrical nanostructures exhibits exceptional thermal conductivity, mechanical and electrical properties. Its ability to exhibit such extraordinary properties stems from combination of the discrete angle created during its roll up and the radius formed. The inability to produce consistently carbon nanotubes that are tailored for specific needs remains a major bottleneck. Moreover, functionalization of carbon nanotubes to enhance their processability is often non-regioselective [50].

Because corannulene has the properties of both fullerenes and benzene, it possesses unique electronic properties more related to fullerenes as well as the ability to be modified like benzene (Fig. 11).

Corannulene has fluorescent properties and organic molecules using its framework could have a large impact on a variety of fields, including the display

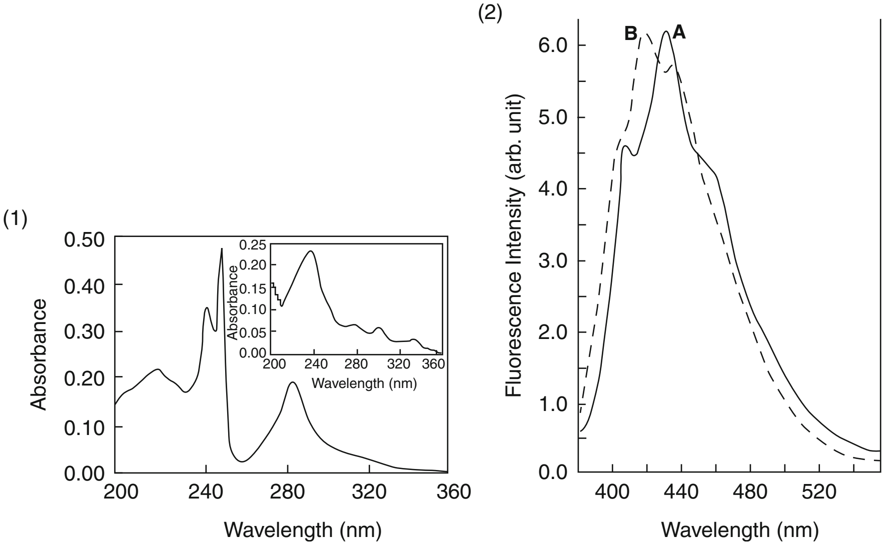


Fig. 12 (**a**) Absorption spectrum of cyclopentacorannulene in cyclohexane. (*Inset*) Absorption spectrum of corannulene in cyclohexane. (**b**) Fluorescence spectra of purified samples of (*A*) cyclopentacorannulene and (*B*) corannulene. Excitation wavelength = 285 nm

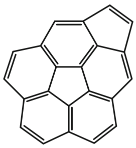


Fig. 13 Cyclopentacorannulene

industry [51]. It has been observed that the phosphorescence and fluorescence of corannulene has a lifetime of 2.6 ns and 10.3 ns, respectively [52]. The corannulene bowl inverts at a rate of approximately 200,000 times per second [53] and the fluorescence and phosphorescence spectra of corannulene is an average of the continuous bowl inversions (Fig. 12). The absorption and steady-state fluorescence measurements of corannulene and cyclopentacorannulene were examined to help determine the spectroscopic properties [54].

Cyclopentacorannulene consists of two additional carbon atoms attached to the outer rim of corrannulene, forming a cyclopentene ring (Fig. 13). The additional carbon atoms extend conjugation and increase rigidity and bowl depth to 1.05 Å (by comparison corannulene has a bowl depth of 0.89 Å). The observed bathochromic shift from corannulene to cyclopentacorannulene can be attributed to the additional π-electrons that extend the overall conjugation of the corannulene ring system. The bathochromic shift of the fluorescence spectrum of cyclopentacorannulene compared to corannulene can also be attributed to the additional π-electrons.

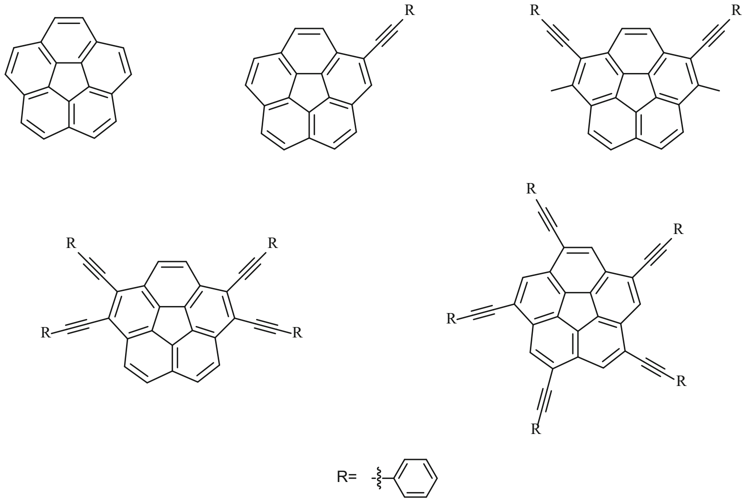
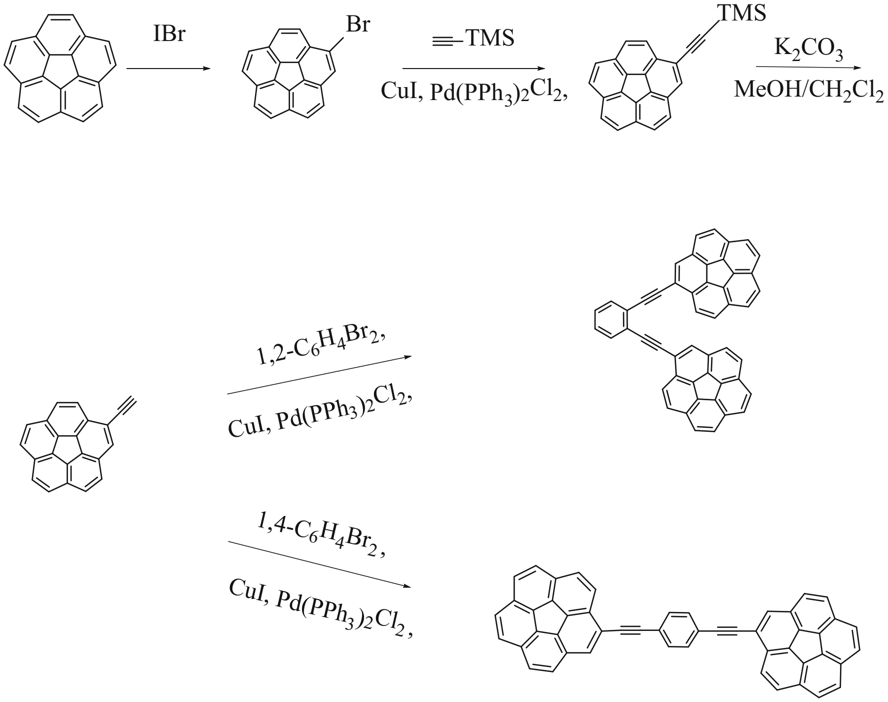


Fig. 14 Comparison study of multiethynylphenyl derivatives of corannulene

However, one major drawback to corannulene and cyclopentacorannulene being utilized as fluorescent materials are their low fluorescent quantum yields of (0.07) and (0.01), respectively. However, unlike fullerenes and nanotubes, linking corannulene with ethynyl bridges does not introduce an sp^3 hybridized carbon. Functionalizing corannulene in this manner allows for the ability to change the HOMO–LUMO gap and thereby changing the fluorescence properties. For these reasons – and many more – it is worth investigating the hidden properties of corannulene which would be highly beneficial in designing systems which could emit blue color with high quantum yields/thermal stability. With the ability to produce larger quantities of corannulene, more has been learned about the photophysical properties of this unique molecule. Bicorannlenylacetylene – an example of a monosubstituted corannulene derivative synthesized by Siegel's group – exhibits strong blue fluorescence with quantum yields of 0.57, more than eight times that of the parent corannulene [55]. However, bicorannulenylacetylene is unstable and quickly decomposes even at $-16°C$. Results clearly show that π-conjugation can be extended between corannulene units if tethered by triple bonds and show predominant red shift (302 nm) in the absorption spectrum. On the other hand, more recent reports from Siegel et al. highlight the expansion of ethnyl derivatives of disubstituted, tetrasubstituted, and pentasubstituted alkynyl corannulene derivatives [56].

Interesting absorption/quantum yield trends of multiethynyl corannulene derivatives have been presented (Fig. 14). Surprisingly, longer wavelength absorption was noticed for tetrasubstituted followed by disubstituted in comparison to highly symmetric pentasubstituted corannulene derivatives. Possible reasons for such an anomaly could be symmetry forbidden transition states and the presence of multiple non-radiative relaxation modes in ground states with higher rates of decay. Meanwhile the Mack group reported the synthesis/photophysical properties of a series of



Scheme 5 Synthesis of 1,2-bis(corannulenylethynyl)benzene and 1,4-bis(corannulenylethynyl) benzene

o, *p*-substituted bis(corannulenylethynyl)benzenes (Scheme 5) [57]. The reason behind their synthesis was to examine the photophysical and thermal properties of these materials in comparison to bicorannuleneylacetylene. Surprisingly, none of these materials showed any signs of decomposition even at 300°C. As expected, both *ortho* and *para* substitution showed enhanced conjugation (299,371 nm).

These findings raise an important question with reference to the nature of linker and corresponding conjugating site. In benzene it is an established fact that groups placed in *ortho* and *para* positions are always in conjugation whereas in *meta* they are not. A detailed investigation related to site specificity on corannulene's rim have to be undertaken in order to understand which substitutions resemble *o*/*p* and *meta*. The data generated from these types of studies would certainly help in designing materials with extremely robust and thermally stable blue LEDs.

4 Conclusion

Corannulene and other fullerene fragments have considerable potential for uses in many applications. These properties can be directly applied to organic light emitting diode (OLED) technology. Improvements in the syntheses of these molecules can potentially make these structures viable building blocks in the development of nanotechnology. As bigger and more diverse carbon-based structures are synthesized, more properties of these unique molecules will be discovered. The development of carbon-based materials will potentially be the bridge between current problems and possible solutions.

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