

# Inter-stellar Space Discovery, Spectroscopic Structure identification and Application of C<sub>60</sub> [Buckminsterfullerene]

Dr. Shalini Jaiswal, Shubham Tiwari, Dr. Preeti Singh Bahadur

Amity University Greater Noida, India

[sjaiswal@gn.amity.edu](mailto:sjaiswal@gn.amity.edu)

**Abstract**— The allotropes of carbon nanostructure material—such as graphite, graphene, diamond, fullerenes, carbon nanotubes, amorphous carbon, and carbyne—have received great interest due to their chemical and physical properties. Each allotrope exhibits different properties depending on its carbon structure and size. Eiji Osawa, a Japanese scientist first found the existence of this form of carbon (Buckminsterfullerene) in 1970. Later in 1985, during work on Carbon clusters, a team of scientists which includes Harry Kroto, Robert Curl and Richard Smalley discovered C<sub>60</sub>. In 1990 a team of astrophysicists led by Wolfgang Kratschmer and Donald Huffman developed a method to produce this molecule in larger quantities.

The Nobel prize committee awarded Harry Kroto, Robert Curl and Richard Smalley were awarded with Nobel Prize in 1996 For the discovery C<sub>60</sub>. These molecules were first detected in space in 2010 and this incident hinted that these so-called Buckyballs could be responsible for the mysterious interstellar absorptions. The other carbon allotrope materials—fullerenes and carbon nanotubes—have quasi-sp<sup>2</sup> hybridization [1]. Unlike graphite or graphene, which are predicted to be in planar geometry in their stable form, spherical fullerene has a pyramidalization angle ( $\theta_{\sigma\pi} - 90$ ) depending on the number of carbon atoms. In this article we focusing on discovery and structure identification of Buckminsterfullerene in space

**Keywords**— Astrochemical modeling, C<sub>60</sub> [Buckminsterfullerene], gas phase data, Matrix data, Fullerenes in space

## 1. Introduction

The other carbon allotrope materials—fullerenes and carbon nanotubes—have quasi-sp<sup>2</sup> hybridization. One example of the pyramidalization angle belonging to C<sub>60</sub> fullerene is 11.6°, which means that a 101.6° angle was formed between the  $\sigma$  and  $\pi$  orbitals in a carbon atom. Among various types of fullerene, the most commonly known and most stable species is Buckminsterfullerene, or C<sub>60</sub>. C<sub>60</sub> fullerene is soluble in non-polar or slightly polar organic solvents. The non-polar solvents, such as toluene, o-xylene, carbon disulfide (CS<sub>2</sub>), dichlorobenzene (DCB), etc., are commonly used to extract the fullerenes from freshly prepared carbon soot after the synthesis process. It is exactly 101 years back from 2020 that two Diffuse Interstellar Bands were first discovered by Mary Lea Heger. Today we know more than 500 Diffuse Interstellar Bands. In numerous observations in labs and studies, maximum effort is applied so as to know about the carriers of what we better know as interstellar absorptions that are observed in the light of red-turning stars crossing the diffuse and translucent clouds. Several claims existed in the past for the specific DIBs over specific fullerene species; any one of those claims did not withstand dedicated follow-up studies. The only explanation was the molecule Buckminsterfullerene. Campbell et al in 2015 showed and proved that two strong bands, recorded in the lab which were around 960 nm, precisely coincided with the known DIBs. And in some of the follow-up studies, we got three more matches between transitions of C<sub>60</sub> and new observational DIB studies were claimed. In these last five years the evidence of the existence of C<sub>60</sub> as the first identified carrier of DIBs - including new laboratory data and these many observations provided to us by the Hubble Space Telescope - has been accumulating, But not all open issues have been solved till this time.

The number of molecules identified in the interstellar medium has exceeded 200 different species in simple or complex molecules. These species have been found mostly in cold (~15 K) dark clouds and around the nearby dead stars. These chemical reactions are driven in both solid and gaseous phases. These reactions can tell us about the chemical compositions of the planetary systems. We got these signals through some radio, infra-red or spectroscopic detections in emission and absorption. Only 10 to 15 species were identified in those translucent clouds and they were satisfied only to some of the smaller molecules. The lower column densities in the diffuse medium limit detection methods mainly to the light based absorption spectroscopy. Typically, those molecules are identified

by watching the absorption features in the light of reddened stars [Stars with light which crosses one or more interstellar clouds on their way to Earth]. At the same time, along many different lines of sight more than 500 unresolved (diffuse) bands have been observed, differing in width and intensity, and covering the range of 400-1000 nm, with a few bands observed in the near infrared region. These bands are the Diffuse Interstellar Bands, DIBs. By their strength, we can say that DIBs must originate from abundant molecular species, but accurate identifications are still not possible; even after the notable progress and development in the technology and development in the laboratories.

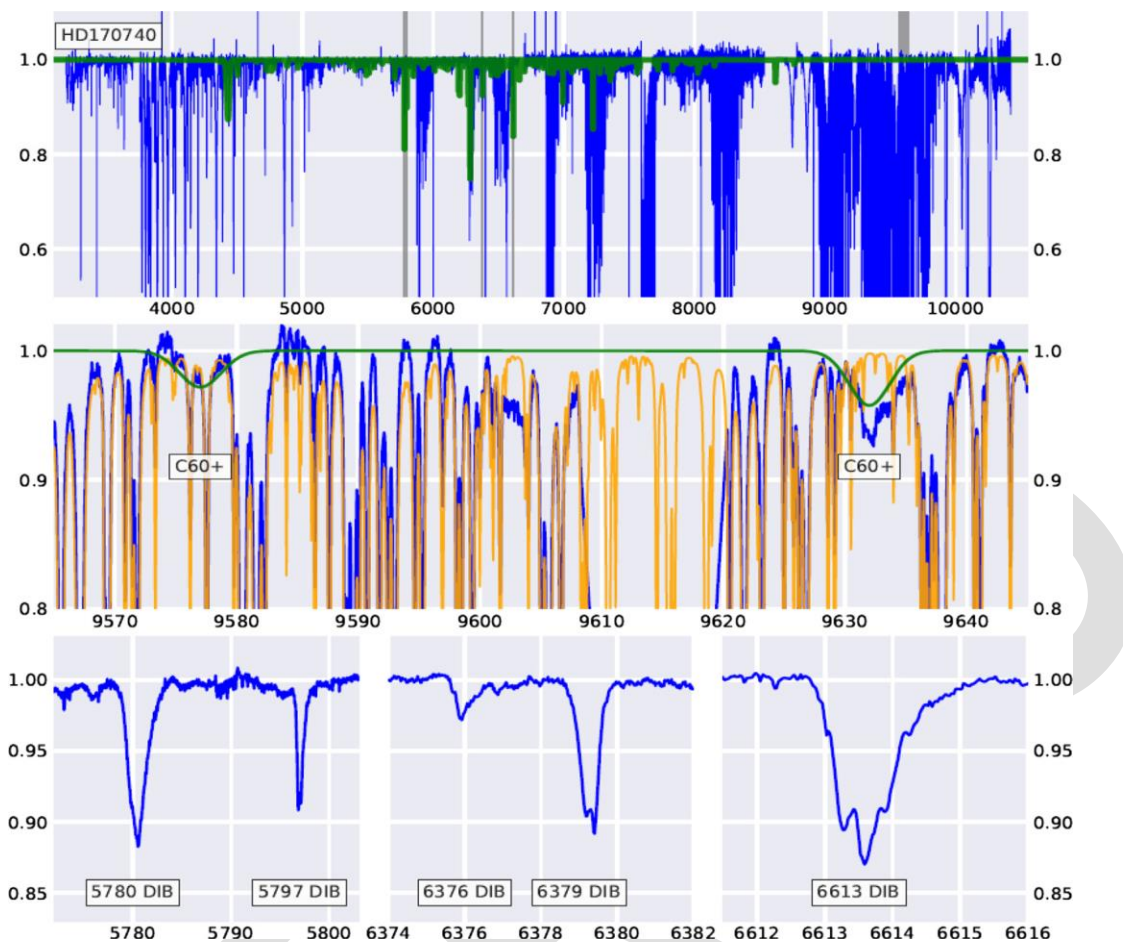
Over all these days, we have collected evidences that are related to DIBs which are related to electronic transitions of the different phase of the gases containing atoms of carbon. For research, many other tracks and carriers have been tested and proposed, varying from carbon chain radicals to polycyclic and the aromatic hydrocarbon cations, and they often gave negative results. This was due to some overlaps, like for  $C^-$ ,  $HC_4H^+$  and  $IC_3H_2$  which came to be coincidental and were shown not the real matches. A remarkable exception is the fullerene cation of  $C_{60}$ , and the result of 25 years of dedicated spectroscopic work, both in the laboratory and in the space through the space telescopes. This remarkable and mysterious  $C_{60}$  molecule was named "Buckminsterfullerene" on its structure similarity with a structure of a famous architect of that time. The architecture was a Geodesic Dome and the name of the architect of that dome was "Buckminster Fuller."

## **2. DISCOVERY OF $C_{60}$ OR BUCKMINSTER FULLERENE AND SPECTROSCOPIC STRUCTURE IDENTIFICATION:**

### **a) DIBs surveys:**

In 1919, Mary Lea Heger observed two broad features when she was studying the interstellar sodium lines towards spectroscopic binaries around 5797 and 5780 angstrom. These bands had their origin in gas and dust of interstellar space. But we still do not know about the exact

nature of those diffused bands. Even after more than 100 years, a lot of DIBs were reported resulting in more than 500 DIBs, mainly in Ultraviolet and Visible spectrum of light extending into the Near Infrared Region. Studies on all these Diffused IBs were mostly focussed on their small numbers and for limited wavelength ranges and also for specific types of astrophysical environments. All of the studies hint that, features due to known interstellar atoms and also the smaller molecules and it can be used as a diagnostic tool to perfectly define the physical conditions in the environment's carrier region. The followed image gives a simple selection of several DIBs, also the sub-structure that has been linked to unresolved rotational contours:



This survey teaches that the high-resolution spectrum allows us to determine accurate peaks and the band profiles (line's shape, intensity etc.). Conducted in a very secure and a controlled condition, this survey was for some exceptional and specific molecules. A good characterization of all these features aids this search for the most likely DIB carrier molecules.

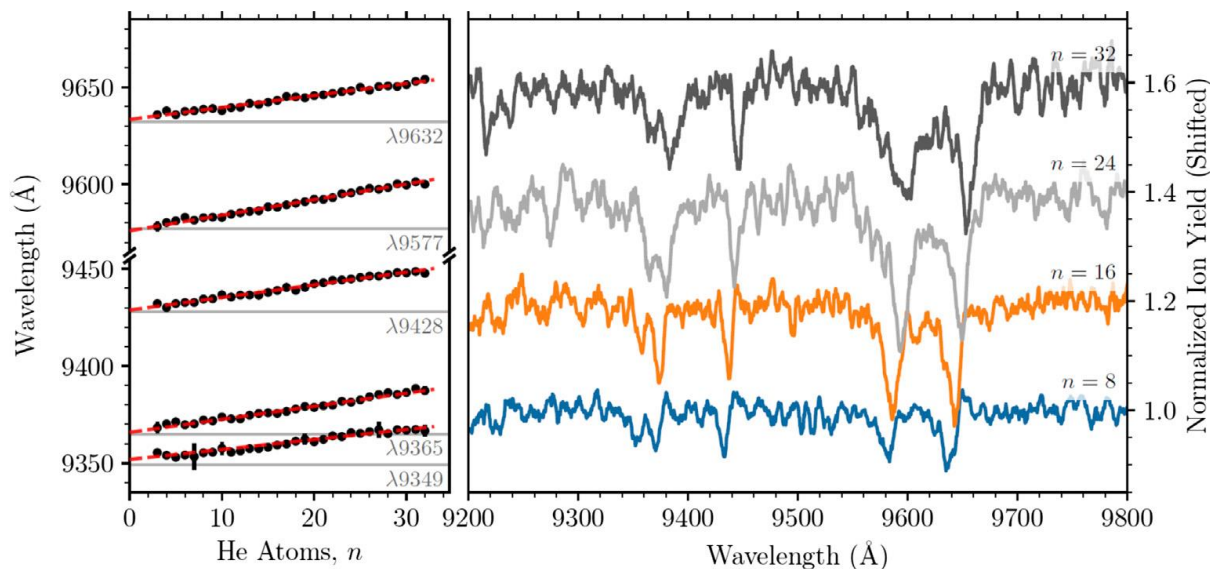
#### b) Matrix data:

DIB carriers can only be given after comparison of astronomical data with their respective spectrum accurately. Diffuse Interstellar Bands cannot have originated from stable molecules as proposed in the late 80s and 90s. Hence the labs preferred to study molecular radicals and ions that could be present in space. With the technology of that time, it was much difficult to generate such species. And here comes our saviour and a real alternative; Matrix Isolation Spectroscopy. In this method the ions can be deposited for a long time according to their masses in a chemically inert and cryogenic (Place with very low temperature [Approx. 4-30 K]) environment; which can result in higher ion density ( $10^{15}$ - $10^{16}$  particles/cm<sup>3</sup>). Foing and Ehrenfreund, two scientists linked two strong absorption bands at  $9580 \pm 4$  and  $9642 \pm 3$  angstrom in 1994. This was recorded for C<sub>60</sub> embedded in rare gas matrices to the possible DIBs. This could be done only in an environment of inertness. Several groups tried to record the corresponding C<sub>60</sub> gas phase spectrum but were unsuccessful every time.

#### Tagging methods and Gas phase data:

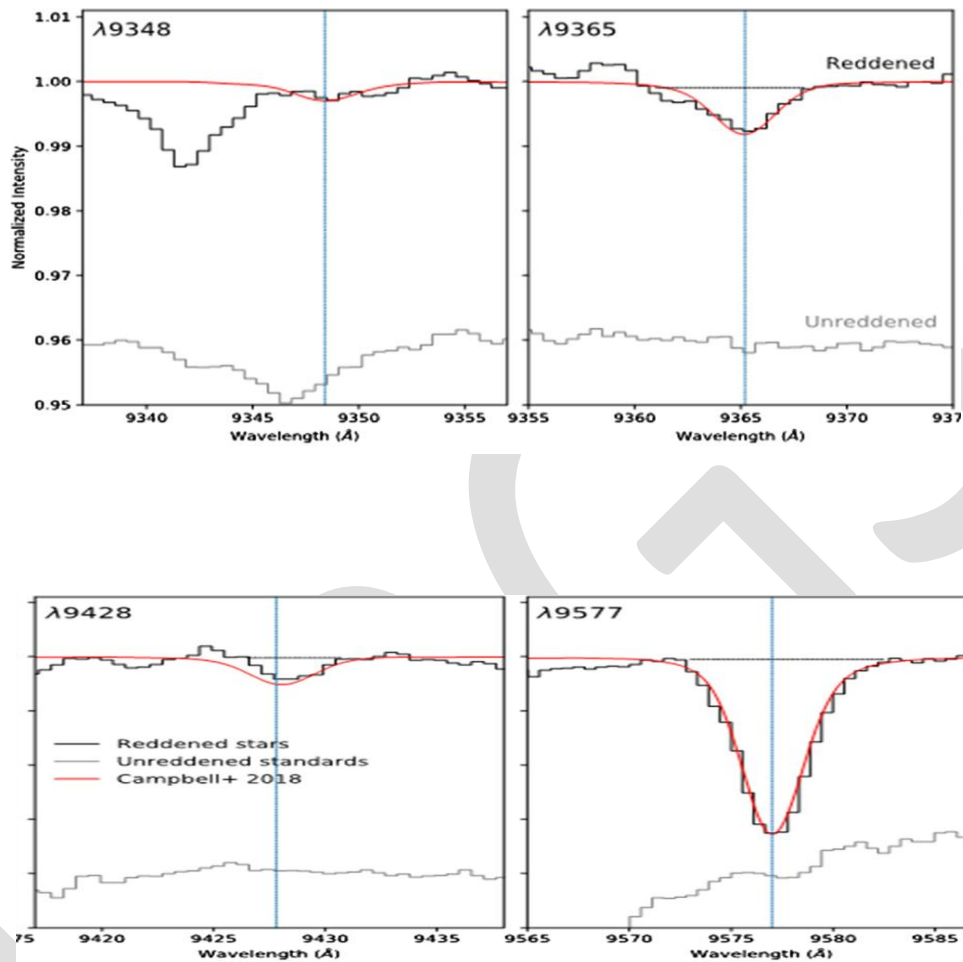
The recording of the real spectrum of the molecule in the gas phase is not easy, as we have seen earlier. For this, we need to take Buckminsterfullerene in the gas phase, ionised with densities high enough to take it in the range of desired spectroscopy observation. After some progress in techniques, they were used to record more precise values in adiabatically cooled plasma expansions, resulting in high resolution electronic spectrum for a long number of pure and hydro-carbon radicals which are all considered to be possible DIB carriers. But this method failed in distinguishing between match and overlap.

In 2015, Campbell Et Al, recorded the spectrum of the  $C_{60}-He_n$ , where  $n = 1$  to 4. This involves iron trap technique. With his co-worker Gerlich, he found that the wavelengths shifted linearly with the number of He-atoms attached to them. This shift was approximately 0.2 angstrom per He-atom.



### c) Ground based and Hubble Telescope observations:

When the availability of  $C_{60}$  was proved in space it became possible to compare the spectrum of Diffuse Interstellar Band with astronomical data accurately with the data of gaseous phase. This comparison between laboratory results and the astronomical data showed convincing overlaps; both in wavelength and bandwidth. They did not observe the bands simultaneously, along one line of sight, but towards different targets. This thing gave rise to a debate; also given the slightly lower signal to noise ratios. It was not claimed that the received detections were real or might be a different result of partly processing of data. Also a discussion was raised that the two strongest  $C_{60}$  DIBs have different intensity ratios. But, in 2000, it was intentionally proved that the intensity ratio is constant within 20% uncertainty which was logical with the assumption that both of the bands originate from the same carrier. Afterwards, Galazutdinov and his mates gave a different set of theories for the substantial number of lines of sight with rather strongly varying intensity ratios. This varying value (9633/9578) is not really expected. By the help of our own Hubble Space Telescope, Cordiner ET Al found the zoomed in view of the line-of-sight spectral regions of the bands produced by the Buckminster fullerenes in interstellar space. The grating settings which were used with the Hubble Space Telescope did not allow the scientists to record two stronger Diffuse Interstellar Bands at the same time. And hence it was not possible to get the accurate results. For this work the group of scientists took help of atmospheric uncertainties in the intensity of DI Bands. Finally, this was done with the  $He^+$  (Helium droplet ion) and the spectral line got out from the Hubble Space Telescope for the  $C_{60}$  spectrum by correcting the shifts. However, the intensity ratios were not directly compared. Instead of that, they were compared through their overlapping bands.

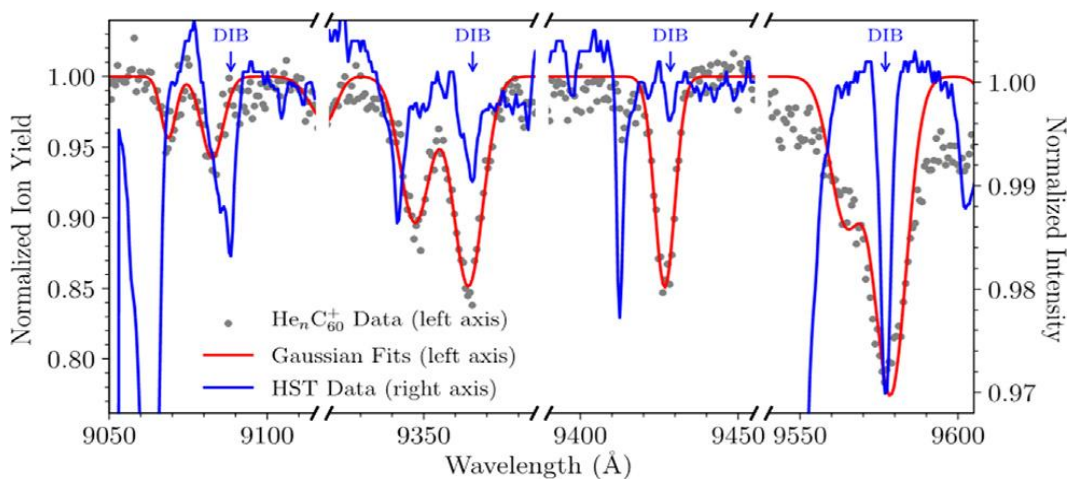


#### e) Astrochemical Modelling:

The Buckyballs exist in space and ionise with the help of the UV Radiations of the stars where they are found. After the electron recombination, they become complete and neutral again. We have also found  $C_{70}$  in space and as a result of that, we can say, there must be a presence of  $C_{70}$  in ionic form. The astrochemical model is there to describe the gap between  $C_3$  and the  $C_{60}$  spectrum.

This idea was given that fullerenes could be formed in a top-down scenario. This takes into consideration a very large amount of polycyclic and aromatic hydrocarbons. The presence of the  $C_{60}$  molecule in space may be the direct consequence of molecular process bowling graphene planes. And may I tell you that the graphene being the thinnest and the most strongest material ever existed and seen by the scientists.





### 3.FULLERENES IN SPACE:

The Noble researchers Kroto, Curl and Smalley got the Nobel prize in 1996 for the discovery of the  $C_{60}$  and the  $C_{70}$  in 1985. Fullerenes were found to be very tough and could be formed in very tough conditions like space. Finally, when the better sensitive devices came after the IR and Visible ray telescopes, it was easily proved that the fullerenes could be in space. This technology was built in the device named Spitzer Space Telescope. Sellgren Et Al gave a detailed research of High-resolution spectrum in range of 15 to 20 micrometres with Spitzer's infrared spectrograph of the reflection nebula NGC 7023. They also found some emission features at 17.4 and 18.9 micrometres and discussed that this could be good due to  $C_{60}$ . In treasure trove of Spitzer's observations, Cami Et Al found the entire spectrum of planetary nebula TC 1. This proved the presence of  $C_{60}$  as well as  $C_{70}$ . Fullerenes are thus indeed widespread and abundant in space – as Kroto had predicted in 1985 came true.

### 4.APPLICATION OF $C_{60}$ OR BUCKMINSTER FULLERENE

$C_{60}$  has been applied in various applications due to its unique chemical and physical properties. These applications include supercapacitors<sup>7,8</sup>, hydrogen

storage<sup>9,10</sup>, nanoelectronics<sup>11,12</sup>, and biomedical applications such as gene and drug delivery<sup>13,14</sup>. Additionally, the quasi-sp<sup>2</sup>-hybridized carbon belonging to  $C_{60}$  supports the high electronic conductivity in charge transportation and separation<sup>15</sup>. Therefore,  $C_{60}$  and its derivatives have many potential uses in optics due to their electron-accepting characteristics and photophysical properties. Due to its unique optical properties,  $C_{60}$  is used in various applications, including solar cells<sup>18,19</sup>, light to electrical energy converters in photovoltaic devices<sup>20-24</sup>, photocatalysts<sup>25-29</sup>, phototherapy<sup>30,31</sup>, bioimaging<sup>32,33</sup>, and biosensing<sup>34,35</sup>.  $C_{60}$  possibly exhibits the optical response depending on the changing of the environment; however, the relevant studies on this sensitive response are still limited.

### REFERENCES:

1. Falcao E.H., Wudl F., Carbon allotropes: Beyond graphite and diamond, J. Chem. Technol. Biotechnol., 2007, 82(6), 524-531.
2. Pierson H.O., Handbook of carbon, graphite, diamonds and fullerenes, 1st ed., William Andrew Publishing, Oxford, 1994.
3. Billups W.E., Ciufolini M.A., Buckminsterfullerenes, VCH Publishers, Inc., New York, 1993.
4. Kroto H.W., The stability of the fullerenes  $C_n$  with  $n = 24, 28, 32, 36, 50, 60$  and  $70$ , Nature, 1987, 329, 529-531.
5. Kroto H., Space, stars,  $C_{60}$  and soot, Science, 1988, 242(4882), 1139-1145.

6. Kroto H., C60 fullerenes, giant fullerenes and soot, *Pure Appl. Chem.*, 1990, 62(3), 407-415.
7. Ma J., Guo Q., Gao H.-L., Qin X., Synthesis of C60/graphene composite as electrode in supercapacitors, *Fuller. Nanotub. Car. N.*, 2015, 23(6), 477-482.
8. Sun Q., Wang Q., Jena P., Kawazoe Y., Clustering of Ti on a C60 surface and its effect on hydrogen storage, *J. Am. Chem. Soc.*, 2005, 127(42), 14582-14583.
9. Yoon M., Yang S., Hicke C., Wang E., Geohegan D., Zhang Z., Calcium as the superior coating metal in functionalization of carbon fullerenes for high-capacity hydrogen storage, *Phys. Rev. Lett.*, 2008, 100(20), 206806.
10. Koiry S.P., Jha P., Aswal D.K., Nayak S.K., Majumdar C., Chattopadhyay S., et al., Diodes based on bilayers comprising of tetraphenyl porphyrin derivative and fullerene for hybrid nanoelectronics, *Chem. Phys. Lett.*, 2010, 485(1), 137-141.
11. Ogawa K., Aoki N., Miyazawa K., Nakamura S., Mashino T., Bird J.P., Ochiai Y., C60 nanowhisker field-effect-transistor application for nano-electronics, *Jpn. J. Appl. Phys.*, 2008, 47(1S), 501-504.
12. Montellano A., Da Ros T., Bianco A., Prato M., Fullerene C60 as a multifunctional system for drug and gene delivery, *Nanoscale*, 2011, 3(10), 4035-4041.
13. Manish K., Kaiser R., C60-fullerenes as drug delivery carriers for anticancer agents: Promises and hurdles, *Pharm. Nanotechnol.*, 2017, 5(3), 169-179.
14. Lai C., Wang M.-M., Zeng G.-M., Liu Y.-G., Huang D.-L., Zhang C., et al., Synthesis of surface molecular imprinted TiO2/graphene photocatalyst and its highly efficient photocatalytic degradation of target pollutant under visible light irradiation, *Appl. Surf. Sci.*, 2016, 390, 368-376.
15. Lai C., Wang M.-M., Zeng G.-M., Liu Y.-G., Huang D.-L., Zhang C., et al., Synthesis of surface molecular imprinted TiO2/graphene photocatalyst and its highly efficient photocatalytic degradation of target pollutant under visible light irradiation, *Appl. Surf. Sci.*, 2016, 390, 368-376.
17. Yi Y., Coropceanu V., Brédas J.-L., Exciton-dissociation and charge-recombination processes in pentacene/C60 solar cells: Theoretical insight into the impact of interface geometry, *J. Am. Chem. Soc.*, 2009, 131(43), 15777-15783. [↑](#)
18. He Y., Chen H.-Y., Hou J., Li Y., Indene-C60 bisadduct: A new acceptor for high-performance polymer solar cells, *J. Am. Chem. Soc.*, 2010, 132(4), 1377-1382.
19. Brown P., Kamat P.V., Quantum dot solar cells. Electrophoretic deposition of CdSe-C60 composite films and capture of photogenerated electrons with nc60 cluster shell, *J. Am. Chem. Soc.*, 2008, 130(28), 8890-8891.
- [20.](#) Hasobe T., Imahori H., Fukuzumi S., Kamat P.V., Light energy conversion using mixed molecular nanoclusters. Porphyrin and C60 cluster films for efficient photocurrent generation, *J. Phys. Chem. B.*, 2003, 107(44), 12105-12112.
- [21.](#) Imahori H., Fukuzumi S., Porphyrin- and fullerene-based molecular photovoltaic devices, *Adv. Funct. Mater.*, 2004, 14(6), 525-536.
22. Baffreau J., Ordonneau L., Leroy-Lhez S., Hudhomme P., Synthesis of perylene-3,4-mono(dicarboximide)-fullerene C60 dyads as new light-harvesting systems, *J. Org. Chem.*, 2008, 73(16), 6142-6147.
- [23.](#) Yamamoto S., Hinoue T., Spontaneous generation of hydrogen gas using a photochemical reaction of fullerene (C60) in the presence of tetraphenylborate in a photovoltaic cell with oil and water phases, *Chem. Lett.*, 2018, 47(6), 744-746.
- [24.](#) Vorobiev A.K., Gazizov R.R., Borschevskii A.Y., Markov V.Y., Ioutsy V.A., Brotsman V.A., Sidorov L.N., Fullerene as photocatalyst: Visible-light induced reaction of perfluorinated  $\alpha,\omega$ -diiodoalkanes with C 60 *J. Phys. Chem. A*, 2017, 121(1), 113-121.

- [25.](#) Apostolopoulou V., Vakros J., Kordulis C., Lycourghiotis A., Preparation and characterization of [60] fullerene nanoparticles supported on titania used as a photocatalyst, *Colloids Surf. A Physicochem. Eng. Asp.*, 2009, 349(1), 189-194.
- [26.](#) Sepahvand S., Farhadi S., Preparation and characterization of fullerene (C60-modified bivo4/fe3o4 nanocomposite by hydrothermal method and study of its visible light photocatalytic and catalytic activity, *Fuller. Nanotub. Car. N.*, 2018, 26(7), 417-432.
- [27.](#) Fu H., Xu T., Zhu S., Zhu Y., Photocorrosion inhibition and enhancement of photocatalytic activity for zno via hybridization with C60 *Environ. Sci. Technol.*, 2008, 42(21), 8064-8069.
- [28.](#) Yi H., Huang D., Qin L., Zeng G., Lai C., Cheng M., et al., Selective prepared carbon nanomaterials for advanced photocatalytic application in environmental pollutant treatment and hydrogen production, *Appl. Catal. B*, 2018, 239, 408-424.
29. Sharma S.K., Chiang L.Y., Hamblin M.R., Photodynamic therapy with fullerenes in vivo: Reality or a dream?, *Nanomedicine*, 2011, 6(10), 1813-1825.
- [30.](#) Mroz P., Tegos G.P., Gali H., Wharton T., Sarna T., Hamblin M.R., Photodynamic therapy with fullerenes, *Photoch. Photobid. Sci.*, 2007, 6(11), 1139-1149.
- [31.](#) Yifeng E., Linling B., Louzhen F., Mei H., Xiaoyan Z., Shihe Y., Electrochemically generated fluorescent fullerene[60] nanoparticles as a new and viable bioimaging platform, *J. Mater. Chem.*, 2011, 21(3), 819-823.
- [32.](#) Liu W., Wei J., Chen Y., Huo P., Wei Y., Electrospinning of poly(1-lactide) nanofibers encapsulated with water-soluble fullerenes for bioimaging application, *ACS Appl. Mater. Interfaces*, 2013, 5(3), 680-685.
- [33.](#) Pilehvar S., De Wael K., Recent advances in electrochemical biosensors based on fullerene-C60 nano-structured platforms, *Biosensors*, 2015, 5(4), 712.
- [34.](#) Afreen S., Muthoosamy K., Manickam S., Hashim U., Functionalized fullerene (C60 as a potential nanomediator in the fabrication of highly sensitive biosensors, *Biosens. Bioelectron.*, 2015, 63, 354-364.
- [35.](#) Chou F.-F., Chang H.-W., Li T.-L., Shih J.-S., Piezoelectric crystal/surface acoustic wave biosensors based on fullerene C60 and enzymes/antibodies/proteins, *J. Iran. Chem. Soc.*, 2008, 5(1), 1-15.