PHOTOPHYSICS OF A NOVEL SYNTHESIZED SHORT-CHAIN DYAD AND ITS NANO COMPOSITES IN CHLOROPLAST ENVIRONMENT

A thesis submitted towards partial fulfilment of the requirements for the degree of

Master of Technology in Laser Technology

Course affiliated to Faculty of Engineering and Technology and
offered by Faculty Council of Interdisciplinary Studies, Law and Management,
Jadavpur University

submitted by

KHALID MEHEBUB
Examination Roll No. M4LST23008
Registration No. 140348 of 2017-2018

Under the guidance of

Prof. Dr. Tapan Ganguly

(THESIS SUPERVISOR)

School of Laser Science and Engineering

Jadavpur University, Kolkata - 700032

School of Laser Science and Engineering

Faculty of Interdisciplinary Studies, Law and Management

Jadavpur University

Kolkata -700032

India

2023

M. Tech in Laser Science & Technology
Course affiliated to
Faculty of Engineering and Technology
and offered by
Faculty Council of Interdisciplinary Studies, Law and Management
Jadavpur University
Kolkata, India- 700032

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I HEREBY RECOMMEND THAT THE THESIS PREPARED BY **KHALID MEHEBUB** UNDER MY SUPERVISION ENTITLED **PHOTOPHYSICS OF A NOVEL SYNTHESIZED SHORT-CHAIN DYAD AND ITS NANO COMPOSITES IN CHLOROPLAST ENVIRONMENT** BE ACCEPTED IN THE PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF TECHNOLOGY IN LASER TECHNOLOGY DURING THE ACADEMIC SESSION 2022-2023.

THESIS SUPERVISOR
Prof. Dr. Tapan Ganguly
School of Laser Science and Engineering
Jadavpur University, Kolkata-7000032

Countersigned

Dr. DIPTEN MISRA
Director
School of Laser Science and Engineering
Jadavpur University, Kolkata-700032

DEAN
Faculty Council of Interdisciplinary Studies, Law and Management
Jadavpur University, Kolkata-700032

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Faculty of Engineering and Technology
and offered by
Faculty Council of Interdisciplinary Studies, Law and Management
Jadavpur University
Kolkata, India-700032

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This foregoing thesis is hereby approved as a creditable study of an engineering subject carried out and presented in a manner satisfactory to warrant its acceptance as a prerequisite to the degree for which it has been submitted. It is understood that by this approval the undersigned do not necessarily endorse or approve any statement made, opinion expressed, or conclusion drawn therein but approve the thesis only for the purpose for which it has been submitted.

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The author hereby declares that this thesis contains original research work by the undersigned candidate, as part of his Master of Technology in Laser Technology studies during academic session 2022-2023.

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NAME: KHALID MEHEBUB

EXAMINATION ROLL NUMBER: M4LST23008

THESIS TITLE: PHOTOPHYSICS OF A NOVEL SYNTHESIZED SHORT-CHAIN DYAD AND ITS NANO COMPOSITES IN CHLOROPLAST ENVIRONMENT

SIGNATURE: DATE:

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KHALID MEHEBUB
Examination Roll No. M4LST23008
Registration No. 140348 of 2017 -2018

THIS THESIS WORK IS DEDICATED TO:

MY BELOVED MOTHER **SHABNAM BANU**, FATHER **ALIDUL ALAM**

MY SUPERVISOR, FRIENDS, SENIORS

ALMIGHTY

AND

SCIENCE & TECHNOLOGY

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1.1. ENERGY

Energy is essential for the existence of all living organisms. We derive a large part of the energy from the sun; hence it is the biggest source of energy for us. The term "Energy" holds various meanings in our daily life, but in Science, it has a specific definition. The word "Energy" is derived from the Greek word "Energia" which means activity or operation. Energy is defined as a physical quantity that is transferred from one object to another to perform work or to heat the object. The S.I. unit of Energy is Joule (J), and it is a derived unit. It is named after the famous physicist James Prescott Joule. When one Newton of force is applied through one meter of distance, then it is said that one Joule of energy is expended.

Our ancestors do know little about the blessings of energy and through time and ages, we gain to know more, understand its capabilities as well as its secure uses in various innovative fields. Energy exist in Universe in various forms. On Earth, that main source is Sun, which we get directly or indirectly [2] except nuclear energy. It is little different because of it can be harnessed by using the atomic properties of atoms or molecules. Geothermal energy is different also. Fossil fuel like coal, petroleum, natural gas that we exploit hugely nowadays are derived from several types of organisms which grew over hundreds to millions years and stored solar energy on planet earth's surface in layers.[3] Renewable energies like biomass, hydro, river water, wind are never ending and is very much needed in today's world more and more.

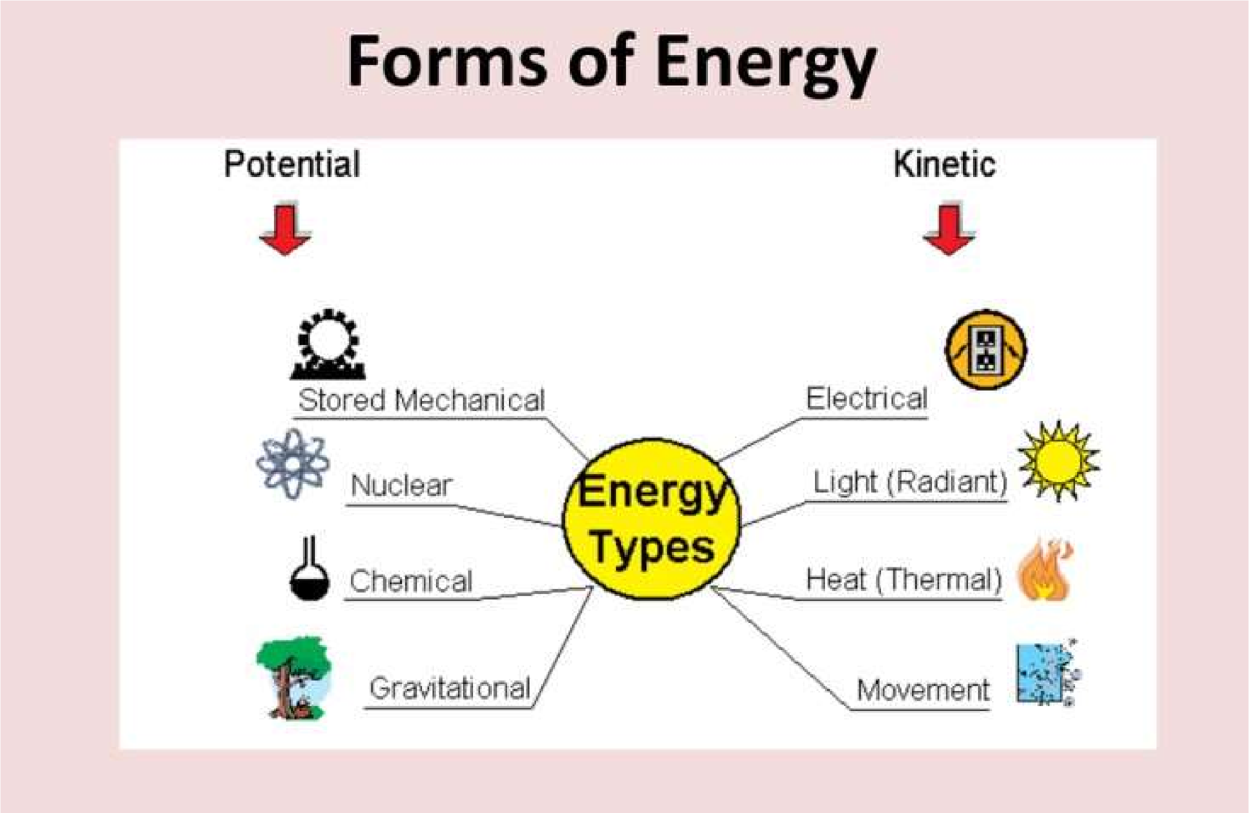


Figure - 1.1: Different Forms of Energy [4]

Physical Properties:

- Energy is invisible in nature, but it can manifest itself through light and wind.
- Sun and stars are the ultimate source [5] of energy.
- The universe has a constant and finite amount of energy.
- Primary energy is a form of energy that is available in nature naturally. For Example, Energy released from the muscles of humans and animals.
- Secondary energy is an energy carrier which is converted by humans from primary energy sources. For Example, electricity is a secondary energy generated from coal, wind and water.
- Energy can vary with the properties such as position, mass, speed, shape, etc.
- In International Systems of Unit (SI), Energy can be measured in Joules (J) which is equal to the work done by one newton force through a one-meter distance [1]. The Dimension of energy is $ML^2 T^{-2}$.

1.1.1. History and Evolution of Energy Sources

The age of stored photosynthesis has been very brief in historical terms. When coal became widely used due to a lack of wood in the late eighteenth century, it was seen as a poor substitute. Late in the nineteenth century, the era of petroleum fuels began. There are three grounds to believe that the current age is coming to an end: resource constraints, environmental challenges, and societal issues. Pessimists now believe that the peak of world oil production was in the year 2000, and that we are already on the downhill slope, according to a special series of energy reports published in New Scientist lately. There are still optimists who believe it will be another 10 years or more, but there is no significant disagreement on the geological fact that, if it hasn't already occurred, the peak of global oil production will occur in most of our lifetimes. Oil will become scarcer and more expensive in that near-future planet. So, while current assumptions are that we will have cheap petroleum for a few decades, we will have to shift the basis of our energy use. Two heroic assumptions underpin this belief. The first is that there will be continued stability in the Middle East, as well as a desire to export oil from the region. The second assumption is that the majority of the world's population will continue to live without the transportation options we take for granted while we waste scarce petroleum resources on such selfish pursuits as car races, jet skis, motor boats, and suburban trips in heavy four-wheel-drive vehicles. As a result, the first and most fundamental argument for shifting away from the current pattern of fuel energy usage is that we are wasting a finite resource, necessitating change.

The use of fossil fuels is causing serious environmental problems at all levels, from local to global. [3] This is the second reason for change. At the local level, urban fuel usage is the primary source of air pollution, which poses major health problems in many large cities (UNEP 2002). In India, Delhi is the city with the most polluted air. The problem of acid precipitation has prompted policy reforms at the regional level to limit sulphur dioxide production as a consequence of fossil fuel consumption (UNEP 2002). The burning of increasing amounts of fossil fuels is the primary source of human-caused climate change on a global scale. Concerns about this situation led to the creation of the Framework Convention on Climate Change and its accompanying Kyoto Protocol, a deal to reduce carbon dioxide and other "greenhouse gas" emissions. According to current scientific consensus, carbon dioxide emissions are around 2.5 times the capacity of natural systems to absorb the gas (IPCC 2001). To put it another way, worldwide fossil fuel consumption needs to be cut by around 40% to bring emissions back into balance with the natural carbon cycle. Climate change, according to recent scientific thought, is speeding up and influencing other planetary cycles, posing a severe threat to human civilization's future. [4]

1.1.2. Energy Statistics in World

China is the world's largest energy consumer, followed by the United States and India. India is an energy importer that consumes about 3% of the world's total energy. It is the world's third-largest coal-producing country, but it still imports more than half of its oil needs. India's energy consumption is growing rapidly, and it is expected to become the world's second-largest energy consumer by 2030. This growth is being driven by a number of factors, including economic development, population growth, and rising living standards. India's energy mix is dominated by coal, but it is also a major producer of renewable energy. The government of India has set ambitious targets for renewable energy, with the goal of achieving 100% clean energy by 2030. India's energy security is a major challenge. The country is heavily dependent on imports for its oil and gas needs, and it is vulnerable to disruptions in the global energy market. The government of India is working to address these challenges by diversifying its energy mix, improving energy efficiency, and developing new energy sources. These efforts are essential to ensuring India's long-term energy security.China ranks first in energy consumption among all countries in the world. If the United States of America (USA) was only inferior to China and ranked second in this race [7]. After China and the United States, India's total energy consumption ranks third in the world. India is an energy importer, consuming about 3% Total energy. India is the third largest coal producer in the world where China the world's largest in this field. Oil provides 30% of India's energy needs, and more than 60% of the oil is imported and most of it comes from the Middle East.

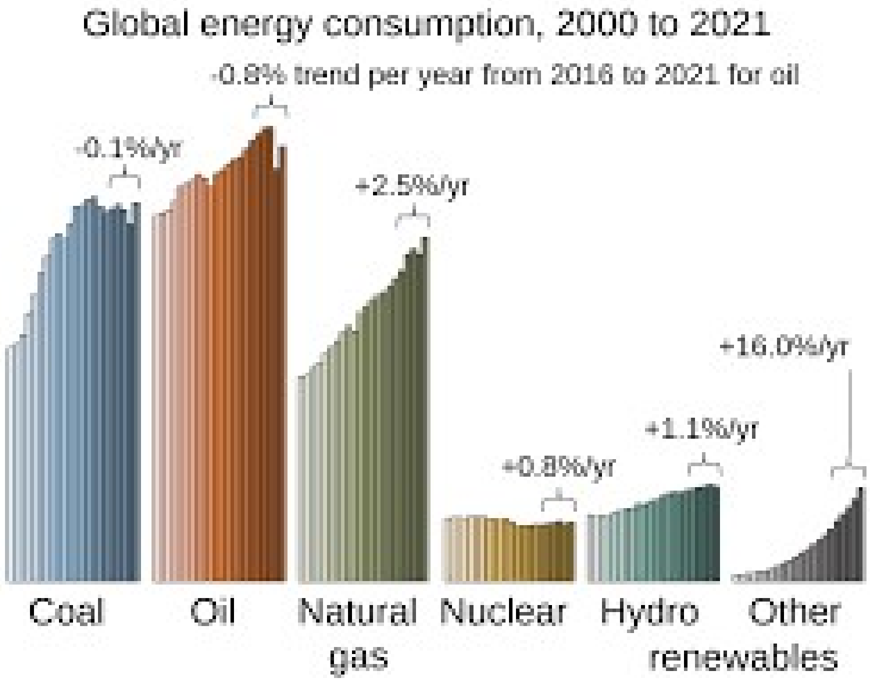


Figure - 1.2. Global Change in Energy Consumption [9]. (Percentages represent change in (2000-21)

Demand for oil transportation has plummeted amid the global health crisis. With 1383TWh producing electricity, India ranks third in the world. According to Ernst &Young's 2021 RECAI (Renewable Energy National Attractiveness Index) ranking India 3. As of November 2021, India has 150 GW of renewable energy capacity including solar (48.55 GW), wind (40.03 GW), small hydro (4.83 GW), biomass (10.62 GW), large hydro (46.51 GW), and nuclear (6.78 GW). India has committed to reaching the target of 450 GW of renewable energy capacity by 2030. The situation must improve everywhere in the world in terms of energy.

1.1.3. Global Annual Average Change in Energy

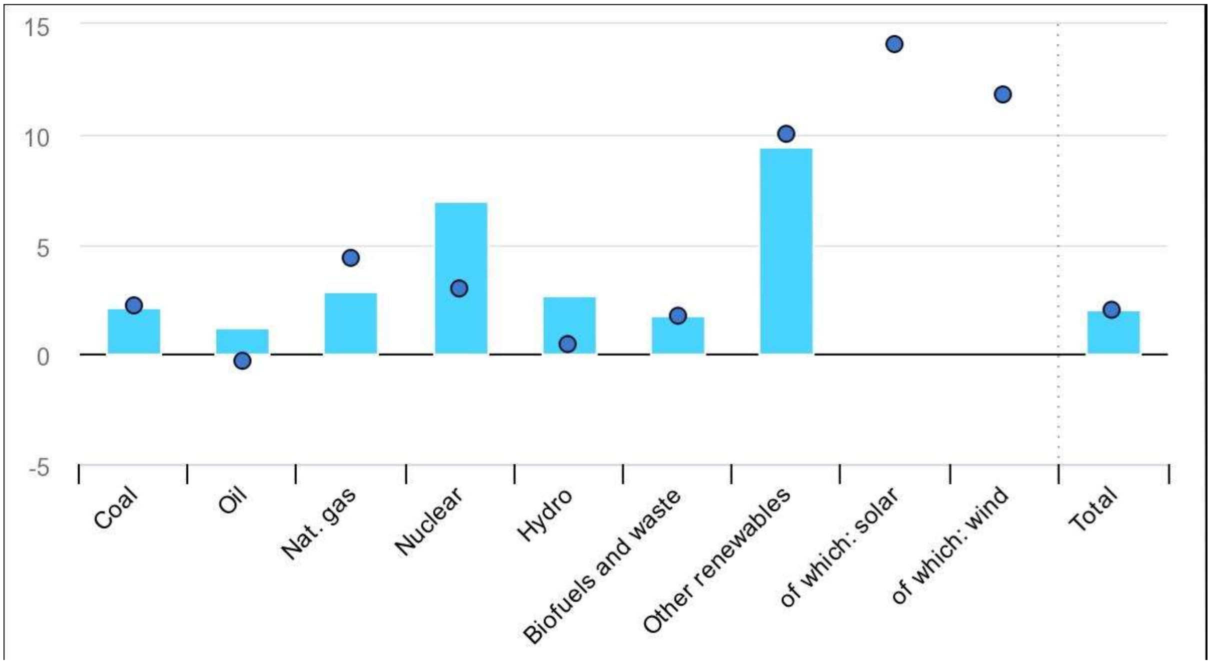
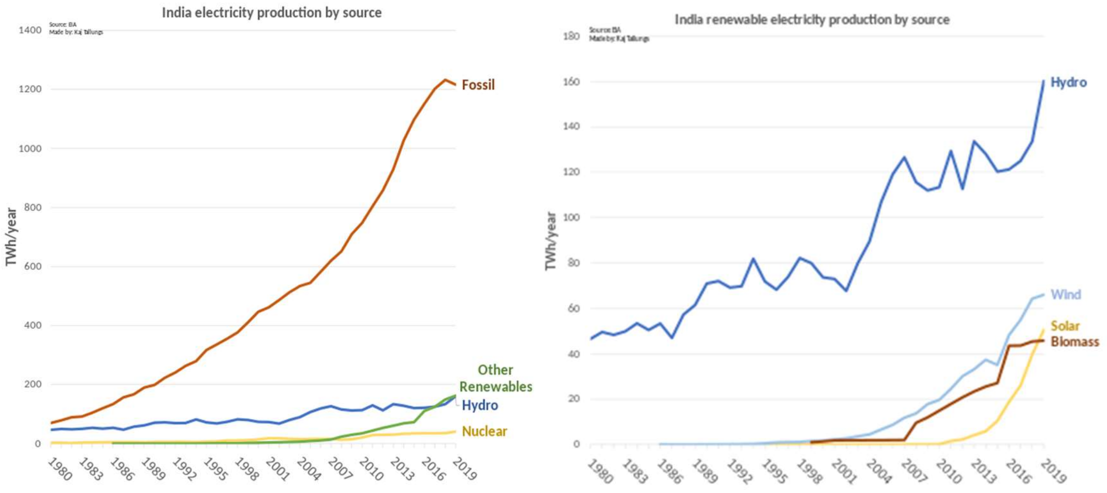


Figure - 1.3: Global Change in Energy.[6] (Deep blue dots represent change in 2019-20)



(i) (ii)

Figure - 1.4: India electricity production (i) by source (ii) by renewable energy [7]

1.1.4. Energy Consumption of India:

As on June 30, 2023 Total Installed Capacity from both fossil fuel and renewable energy sources are tabled below. [5]

1. Fossil Fuel:

Energy Source	Consumption (Billion Units)	Share (%)
Coal	724.5	48.1
Oil	355.2	23.9
Natural Gas	68.2	4.6
Electricity	365.7	24.4
Biomass	94.4	6.5
Other	10.1	0.7
Total Fossil Fuel	2,36,109	59.1%

2. Non-Fossil Fuel

RES (Incl. Hydro)	1,56,608	39.2%
Hydro	46,723	11.7 %
Wind, Solar & Other RE	1,09,885	27.5 %
Wind	40,358	10.1%
Solar	53,997	13.5%
BM Power/Cogen	10,206	2.6%
Waste to Energy	477	0.1%
Small Hydro Power	4,849	1.2%
Nuclear	6,780	1.7%
Total Non-Fossil Fuel	1,63,388	40.9%

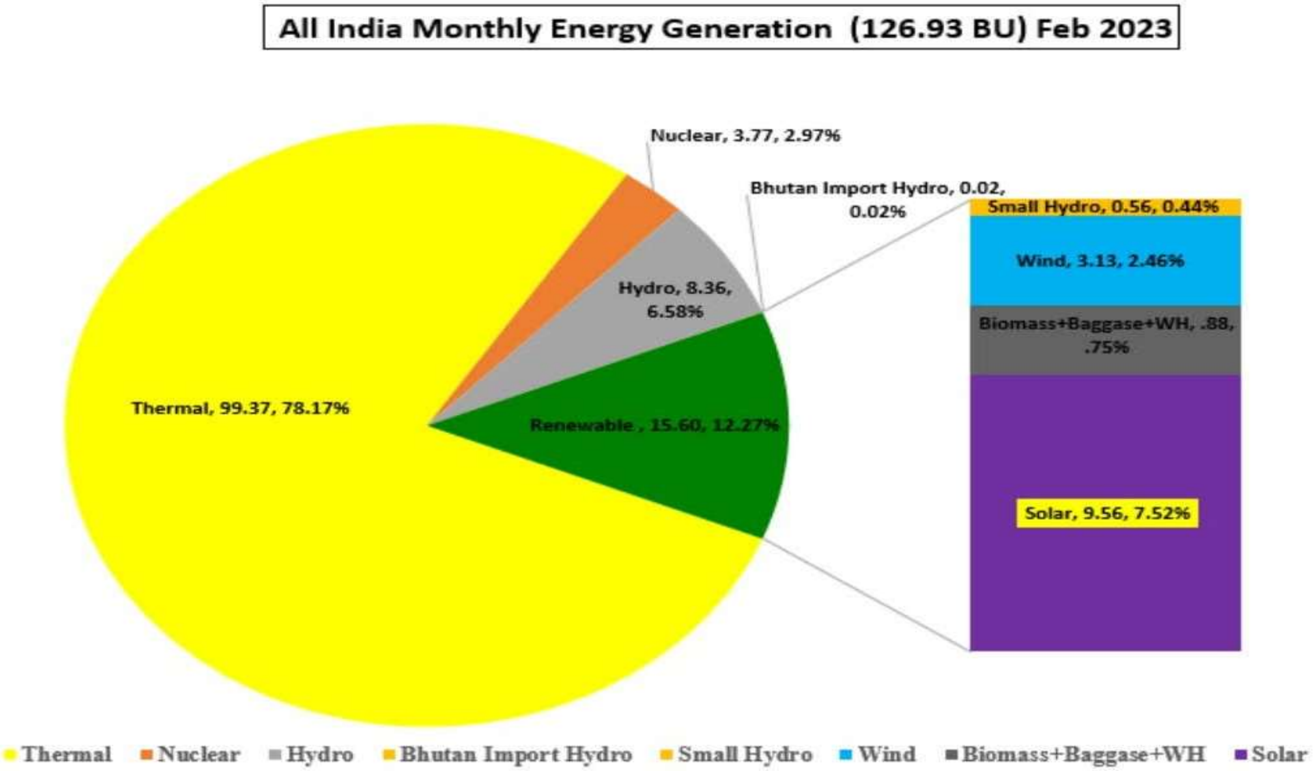


Figure - 1.5: Total Energy Generation in India and Share of Renewable Energy in the month of February- 2023[10]

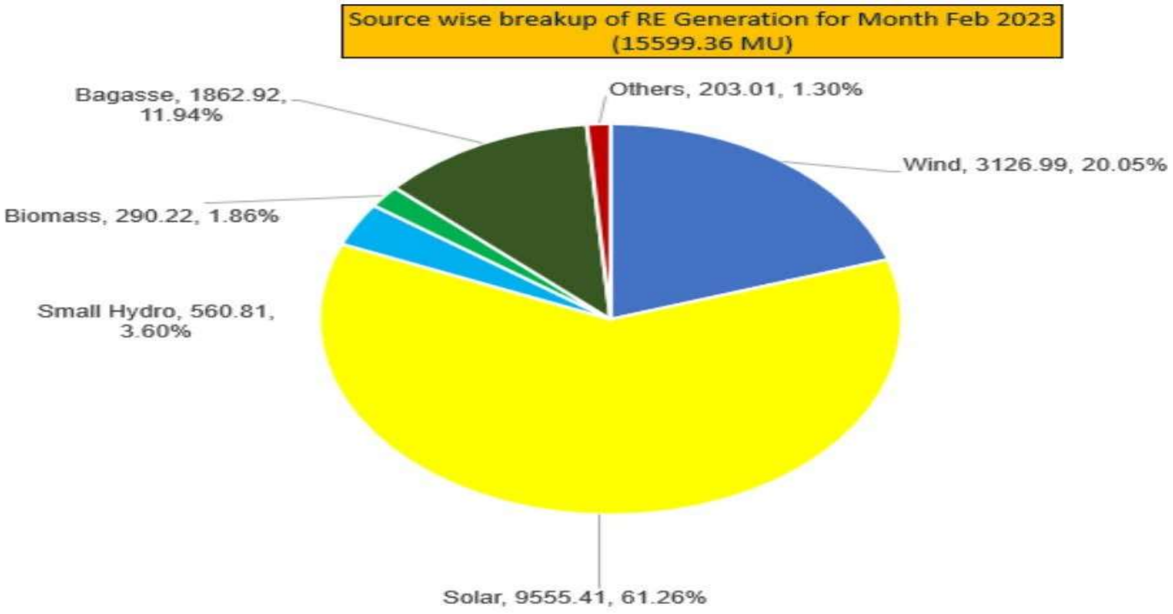


Figure - 1.6: Source wise breakup of RE Generation in the month of February2023 [10]

1.1.5. Energy Crisis

Fossil fuels are a finite resource that is becoming increasingly expensive and difficult to extract. They also produce greenhouse gases that contribute to climate change. As a result, we need to start finding alternative sources of energy that are cleaner, more sustainable, and affordable.

Some of the alternative sources of energy that we can use include solar, wind, hydroelectric, and nuclear power. These sources of energy are all renewable, meaning that they will never run out. They are also cleaner than fossil fuels, and they do not produce greenhouse gases.

The transition to alternative sources of energy will not be easy, but it is necessary. We need to start investing in these technologies now so that we can be prepared for the future.

Transitioning from fossil fuels to renewable and sustainable energy sources is imperative due to various compelling reasons. Fossil fuels contribute to climate change by releasing greenhouse gases, causing global warming and extreme weather events. They also generate air pollution, leading to respiratory health issues. Additionally, fossil fuels are finite resources, depleting with increasing consumption and subject to price volatility. Overreliance on fossil fuels poses energy security risks due to geopolitical tensions and supply disruptions. In contrast, renewable energy offers economic opportunities, technological advancements, and environmental conservation. It ensures resilience to price shocks, provides global energy access, and fosters long-term sustainability for future generations. By embracing sustainable energy, we address these concerns and pave the way for a greener and more sustainable future.

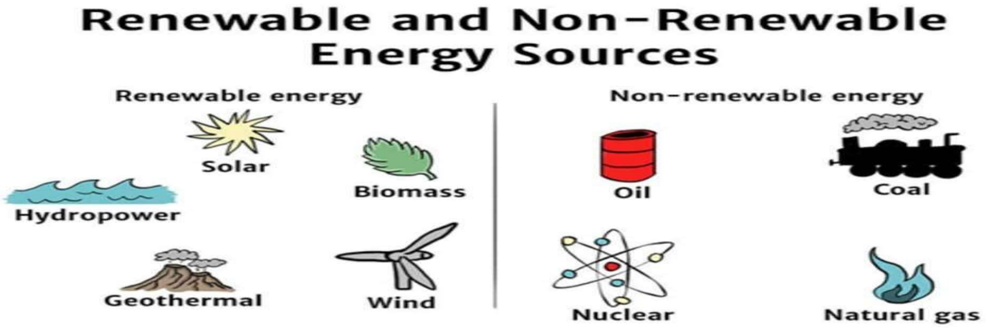


Figure - 1.7: Renewable and Non-Renewable Energy [11]

1.1.6. Solution to Energy Crisis

1. Renewable energy is clean energy, beneficial to the environment, and does not cause pollution. Solar, wind, hydroelectric, geothermal, and other energy renewable energy is one of them. Power generation has rapidly moved from traditional to renewable, due to the benefits and promising future.

2. The study of photochemistry focuses on the fundamental processes that capture and convert solar energy into chemical energy or electricity. He relates to a chemical change caused by the absorption or emission of light or ultraviolet radiation [6] molecule transition from ground to excited state after absorbing a photon (a light particle). The light is done by photochemical reactions. If a molecule loses its chemical identity as the result of photoelectron photochemistry, this process is called photochemistry; whether the molecule retains its chemical identity, this process is called optics physics. Photosynthesis, the technique by which plants obtain energy from sunlight, is a well-known photochemical reaction. Therefore, different types of artificial photosynthesis are really fighting for the right to capture incident photons and use them for the benefit of the community.

3. Nanotechnology offers a wide range of solutions for many problems and improves the current situation, for example, in health care, defence system, and during the energy crisis. Traditional silicon-based solid-state solar cells are one of the few commercially accessible systems for solar energy conversion energy into electricity. Although performance is not so important, quantum dots (Nano scale particles) can be used instead. The good thing is these devices can be made in both normal and room environment temperatures. Efficiency improved to about 9-11%. Ability distribution of quantum dots in different materials, resulting in low-cost, large-area solar cells that could be applied to buildings or vehicles, perhaps the most interesting aspect of quantum dot solar cells [10].

4. Because hydrogen is clean, flexible, and mobile, scientists believe it is an effective means of reducing the world's dependence on carbon-based non-renewable fossil fuels.

5. Photosynthesis is a natural but very advanced method performed by plants. It consists of several chemical reactions and mainly absorbs sunlight for nutrient synthesis. Besides providing us with

food and all other nutrients, all fossil energy today comes from photosynthetic organisms that harvest sunlight. Photosynthesis is broken down into several important steps parts and elements.

6. Antenna system: To absorb light and transport the necessary excitation energy to the reaction centre, where charge separation takes place, photosynthetic organisms employ their internal antenna systems.

7. Reaction factor: With a small amount charge worked in back actions, the reactivity centre produces a stable charge separation system.

8. Oxidation: The oxidation of H_2O molecules is driven by charge separation [8].

Finally, the result is the formation of glucose and oxygen.

9. Artificial photosynthetic systems would be a major advance in energy production and a critical development in tackling the escalating environmental concerns brought on by the over use of fossil fuels [12].

The creation of solar cells is an interesting strategy to address this challenge.

Dyesensitized solar cells have thereby become a practical substitute for pricey solid-state solar cells. There would be ongoing developments, which this thesis will outline.

10. Based on the creation of organic molecular systems that would offer photosensitized processes like PET, or photo induced electron transfer, several more intriguing methods of artificial photosynthesis have evolved in recent years [12]. In previous years, some chemical methods for creating model molecules for synthetic photosynthesis have been proposed [13, 14].

11. The idea of developing a charge storage and artificial light energy conversion device is inspired by the photosynthesis phenomena. Solar energy is to be collected and transformed into usable forms of energy based on the underlying scientific principles of natural processes, such as photosynthesis. A brand-new organic short chain dyad called NNDMBF was created and studied. [15]. By coupling this organic dyad with various noble metals, metal-semiconductor core/shell Nano composite, and ultimately graphene hybrid materials, the basic objective is to build storage systems that resemble super capacitors. The current thesis centres on a current issue in the study of a novel solar cell that converts light energy by using charge electron injection separation in a short chain dyad.

12. This photosynthesis phenomenon raises the possibility that studies on UV-vis absorption, steady state, and time-resolved spectroscopic properties of this newly synthesized dyad in its pristine form and when combined with graphene quantum dots (GQD), graphene oxide (GO), and reduced graphene oxide (RGO) were conducted in various environments. According to steady-state observations, charge-separated species appear in both the ground and excited states when the two redox components are related to a short chain. The short-chain organic dyad system could be coupled with GQD, GO, and RGO to create a highly reliable, affordable artificial light energy converter that is both safe and biocompatible. We need to comprehend these nanostructures' entire potential for energy storage in order to fully utilize them. Thank you so much, sir, for your kind information.

1.2. Photophysical and Photochemical Studies and Processes

The development of life on Earth and the environment around it is greatly influenced by photophysical and photochemical processes. Thanks to a sophisticated set of photochemical and photophysical processes, simple cells evolved into autotrophs, provided the necessities of life, stored solar energy in the form of fossil fuels, and continue to provide us with the majority of our food. The composition of elements in interstellar space and the production of pollutants in the atmosphere are both significantly influenced by photochemistry. Their impact on nanotechnology as well as chemical, physical, biological, and medical sciences and technologies is expanding quickly.

Chemical processes are dealt with in photochemistry.[12] These processes resulted in the UV, or ultraviolet, or infrared, radiation (wavelength, 100-400 nm), or visible light (wavelength, 400-750 nm), being absorbed.

1.2.1. Ground States & Excited States

Electronic reports i.e., ground state (g.s) and excited state (e.s) of a molecule are obtained by considering the properties of all electrons in the unfilled shell. The electronic structures of states are usually expressed by their multiples, singlet (S) or triplet (T). At natural temperatures and in normal environments, most organic molecules, i.e. all electrons, are paired. Pauli's exclusion formula states that electrons will have opposite spins in a pair. When one of an electron pair is promoted to a higher energy orbital, the two electrons no longer share the orbital and the promoted electron can have the same spin as the previous spin or vice versa. A quantum state in which two unpaired electrons have the same spin is called a triplet (T), while a quantum state in which all spins are paired is called a singleton (S).A molecule is moved from the ground state to the electrically excited state by excitation of light with a photon of sufficient energy. Each excited state has its own physical and chemical properties due to light excitation. Photochemical and photochemical processes are those in which excited species dissociate, rearrange, isomerize, or react with any other molecule.

1.2.2. Deactivation Processes in Excited States

Radiative transitions, in which the excited molecule emits light in the form of fluorescence or phosphorescence and returns to the ground state, and intramolecular non-radiative transitions, in which some or all of the energy of the absorbed photon is eventually converted to heat are examples of photophysical processes. The schematic diagram is expressed elegantly by Jablonski Diagram [13]

Physical relaxation processes may be categorized as:

1. **Intramolecular**: These processes are
   - I. Radiative transitions: In this e.m radiation is emitted when excited molecule happens to go to ground state. Fluorescence & phosphorescence are collectively known as luminescence.
   - II. Radiation-less transitions: In this no emission of e.m radiation is occurred during relaxation process.
2. **Intermolecular**: These processes are
   - I. Vibrational Relaxation: Excess energetic molecules in excited vibrational level undergoes very rapid collision with each other or with lowest vibrational energy level in solvent molecule of a defined electronic level.
   - II. Electron Transfer: A photo excited donor molecule interacts with a ground-state acceptor molecule in this reaction. The excited donor is quenched as an ion pair forms, which may undergo back electron transfer.
   - III. ET: Energy Transfer: By transferring energy to another molecule (the acceptor), the donor's electrically excited state is deactivated to a lower electronic state, while the acceptor is promoted to a higher electronic state.

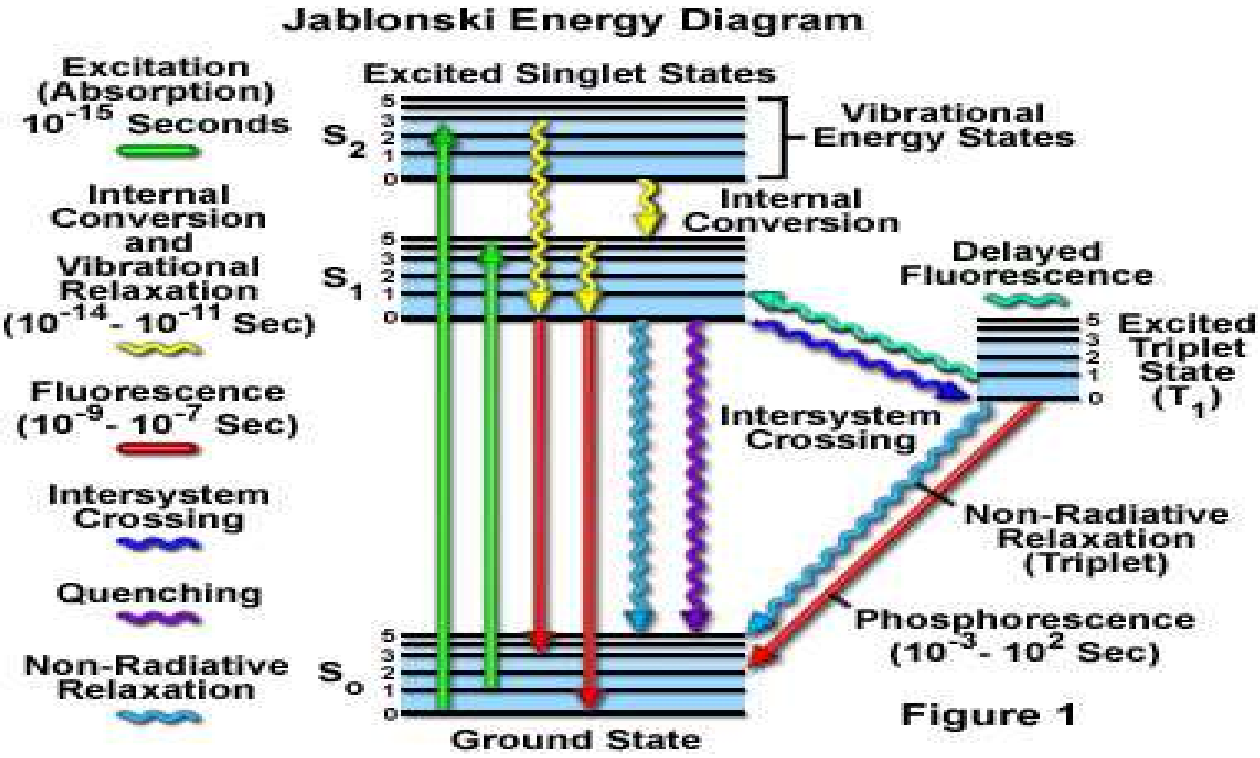


Fig. 1.8: Jablonski Energy Diagram: Physical deactivation of excited states [13]

1.2.3. Laws of Photochemistry:

Absorption: When an atom in a ground or lower level absorbs a photon with energy, E=hν (frequency ν) and moves to an upper level is called absorption.

There are several governing laws regarding absorption of light. They are called laws of photochemistry.

a) First Law of Photochemistry: Grotthuss-Draper Law

Grotthuss-Draper Law states that Photochemistry requires the absorption of light. This is a basic notion, yet it is essential for properly conducting photochemical and photo biological investigations. Due to its fundamentality, it is named as first law of photochemistry. Only light that is absorbed by a molecule can cause photochemical changes in the molecule, according to this theory [14].

b) **Second Law of Photochemistry: Stark-Einstein's Law**

Stark-Einstein's Law states that only one molecule is activated for a photochemical reaction for every photon of light received by a chemical system. It's the second photochemistry law. It also states that just one molecule is activated for a subsequent reaction for each photon of light received by a chemical system. Only one molecule is activated for a photochemical reaction for each photon of light absorbed by a chemical system[9].Albert Einstein developed the quantum theory of light and came up with this 'photo-equivalence law'.

c) **Lambert's Law**

When a ray of monochromatic light goes through an absorbing material, the intensity of the ray falls exponentially as the absorbing medium's length grows**.** This is known as Lambert law [9]. Mathematically it can be written as,

$$I = I_0 e^{-kx}$$

I, I_0 denotes Intensity of transmitted and incident light respectively
and 'k' is absorption coefficient.

d) **Beer-Lambert Law:**

Beer–Lambert law, also known as Beer's law is a relationship between light attenuation and the qualities of the substance through which it travels. The law is extensively used in chemical analysis measurements and in physical optics to understand attenuation for photons, rarefied gases. The modified form of Lambert's law comes from the consideration that decreasing rate in intensity of monochromatic light falls exponentially with the length of the medium as well as concentration (c) of solution.

$$I = I_0 e^{-\varepsilon c x}$$

ε = molar absorption coefficient or molar extinction coefficient

When an atom is in an excited state, it can decay to a lower energy state by emitting a photon. This process is called spontaneous emission. The frequency of the emitted photon is equal to the difference in energy between the two energy states. The phase and direction of the emitted photon are random.

Stimulated emission is a process in which an atom in an excited state is stimulated by a photon to emit a photon with the same frequency, phase, and direction as the stimulating photon. The stimulating photon does not have to have the same energy as the emitted photon, but it must have a frequency that matches the energy difference between the two energy states of the atom.

Stimulated emission is the basis for lasers. When a laser is pumped with energy, it causes many atoms to be excited to a higher energy state. These atoms then emit photons in all directions. However, if a photon with the correct frequency is present, it can stimulate the emission of more photons, which in turn can stimulate the emission of even more photons. This process can lead to a cascade of photon emission, which is what makes lasers so powerful.

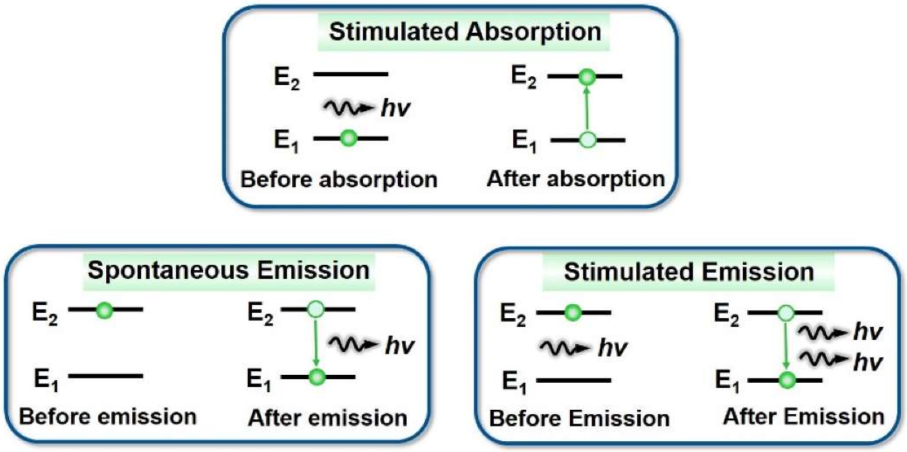


Figure - 1.9: Mechanism of the interaction between an atom and a photon [14]

1.2.4. Franck Condon Principle:

In spectroscopy and quantum chemistry, the Franck–Condon principle describes the intensity of vibronic transitions. Vibronic transitions are changes in a molecule's electronic and vibrational energy levels that occur simultaneously as a result of the absorption or emission of a photon of sufficient energy. The principle states that if the two vibrational wave functions overlap more considerably during an electronic transition, a change from one vibrational energy level to another is more likely to occur [26].

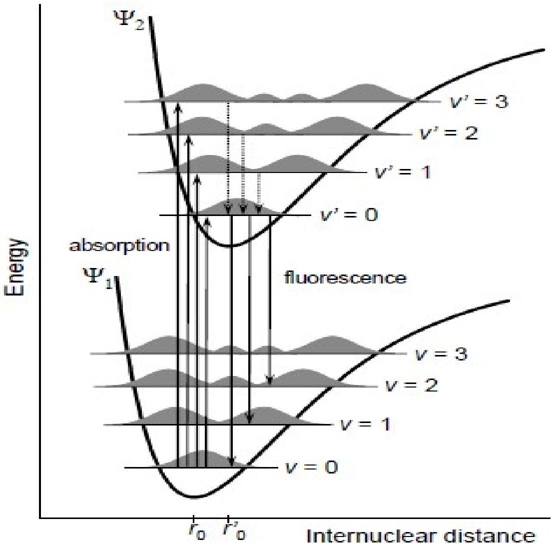


Figure - 1.10: Diagram depicting Franck-Condon principle& absorption, fluorescence emission processes [26]

Quantum Efficiency

The term quantum efficiency (QE) commonly refers to incident photon to converted electron ratio. In photochemical reaction it defines the efficiency of that reaction. For this photochemical reaction, QE need to be unity.

$$\text{QE} = \frac{no.\ of\ molecules\ reacted/sec}{no.\ of\ photo\quad absorbed/sec}\ ;\ \text{QE} = \frac{rate\ of\ chemical\ reaction}{quanta\ absorbed/sec}$$

(Theoretically) **(Experimentally)**

1.3. Light Energy Conversion Process By Dyads

Some donor-acceptor dyads and triads have been synthesized for light harvesting assemblies. Photosynthesis is the fundamental principle of these dyads and triads. Because the donor-acceptor system containing Chlorophyll a and porphyrin can attain a long-lasting charge separation state, it can mimic the photo-induced electron transfer process of natural photosynthesis. Some nanoparticle has clever features that protect charge separation species in diverse stimulated short chain dyads systems by limiting the energy-draining charge recombination process. [9]

Many model compounds with electron donors and acceptors coupled by covalent bonds have been created for use in light emitting diodes (LEDs), photovoltaic cells, organic solar cells, and artificial or model photosynthetic systems, among other things. The creation of numerous effective light energy conversion devices will be aided by the use of synthetic compounds in the form of organic dyad systems with electron donor and acceptor moieties connected together by short spacers. The short-chained dyads may efficiently harvest light, transfer excitation energy, transfer electrons, and produce long-lived charge-separated states. Several strategies were employed on model donor–acceptor connected dyads or multichromophoric systems to boost the charge-separation rate in order to develop various light energy conversion devices. [15]

NNDMBF– A short-chain dyad containing the electron donor 4(N,N-dimethylamine) Benzaldehyde (NNDMB) and the acceptor F (fluorene) has been synthesised. The dyad is shown in following figure. [16]

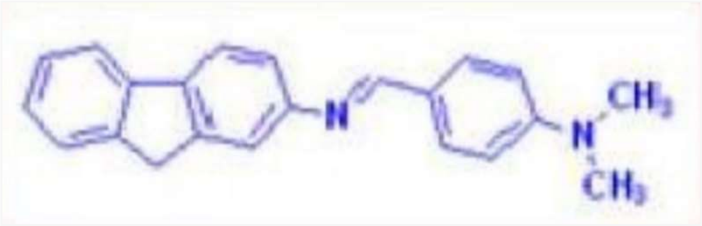


Figure 1.11: Novel short-chain dyad (NNDMBF) [16]

1.4. Graphene

1.4.1. Introduction

Graphene is allotropes of carbon. This name was introduced by Boehm, Setton, and Stumpp in 1994. [17] Graphene is a hexagonal lattice monolayer of carbon atoms. It is a two-dimensional material made up of carbon atoms that have been sp2 hybridized. It has a bond length of 0.142 nm. It has received a great deal of interest in recent years due to its unique electrical, optical, magnetic, thermal, and mechanical properties, as well as its large specific surface area. Because graphene is widely utilized in nanoelectronics, producing high-quality graphene is critical. Geim and Nosovelov synthesized single layers of graphene in 2004 by mechanically cutting a graphite crystal. Graphite is made up of layers of graphene stacked on top of each other with an interplanar spacing of 0.335 nm. Van der Waals forces hold the individual layers of graphene in graphite together, which can be overcome during graphene exfoliation. In terms of thermal and electrical conductivity, graphite has a remarkable anisotropic behaviour Graphene has some distinguishing characteristics that set it apart from other carbon allotropes. It is roughly 100 times stronger than the strongest steel in terms of thickness, but its density is much lower. This material conducts heat and electricity exceptionally well and is nearly translucent. Graphene has a huge and nonlinear diamagnetism, which is stronger than that of graphite and can be levitated by Nd-Fe-B magnets. Graphene possesses exceptional electrical, chemical, mechanical, thermal, and optical properties, making it a critical material in the twenty-first century. It is also touted as the 'thinnest' material in the world. Graphene is presently used in a variety of applications such as energy storage materials, super capacitors, Nano electronics, drug delivery systems, polymer composites, liquid crystal devices, biosensors, and many more. [18]

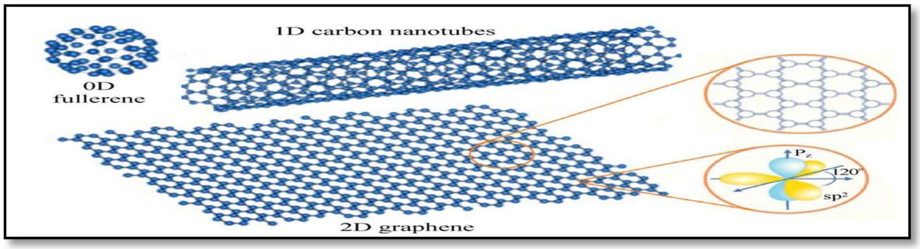


Figure 1.12: Graphene structure [18]

1.4.2. Graphene Quantum Dots (GQD)

Graphene quantum dots (GQDs) are a type of 0D material formed from small fragments of graphene. Due to quantum confinement and edge effects, GQDs display new phenomena akin to semiconducting QDs. Graphene and similar materials utilised for chemical sensing, such as GO or RGO, offer a lot of potential. This is owing to the 2-dimensional structure, which provides a large sensing surface per unit volume and low noise in comparison to conventional solid state sensors

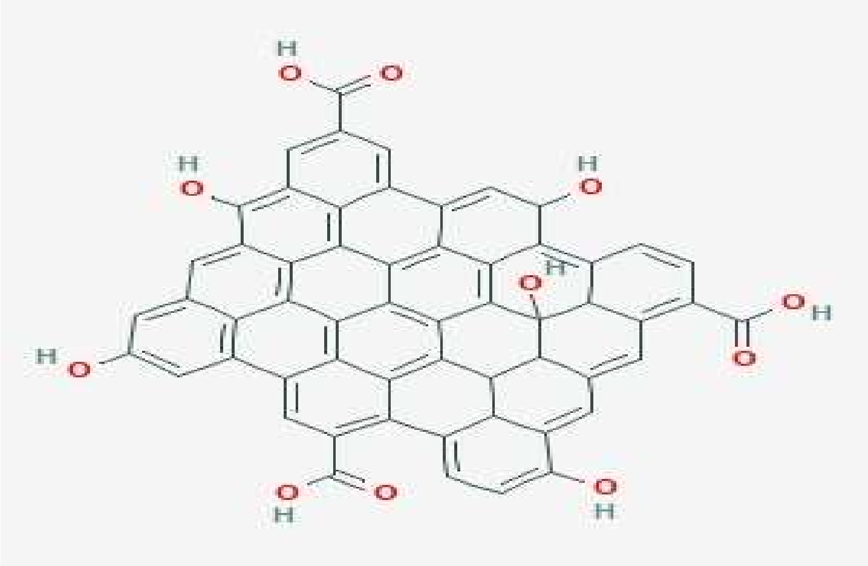


Figure - 1.13: Molecular Structure of GQD. [20]

Properties:

1. GQD consist of one or a few layers of graphene and are smaller than 100 nm in size.
2. Less toxicity, having quantum confinement property.
3. They are chemically and physically stable,
4. GQD has large surface to mass ratio
5. It can be dispersed in water easily due to functional groups at the edges.
6. Fluorescence emission of G-dots has broad spectral range, includes IR, visible and UV.

1.4.3. GQD Synthesis Method:

A variety of approaches have been created to make GQDs.[20] These methods are usually classified as either top down or bottom up. Different techniques, such as graphite, graphene, and carbon nanotubes, were used to turn bulk graphitic materials into GQDs via top-down methodologies. Electron beam lithography, chemical oxidation, graphene oxide (GO) reduction, ultrasonic assisted exfoliation methods are some of the more useful ones. [21] Because of strong mixed acids are used in top-down methods, substantial purification is frequently required. Bottom-up techniques, on the other hand, construct GQDs from small organic molecules such as citric acid and glucose. The biocompatibility of these GQDs is improved.

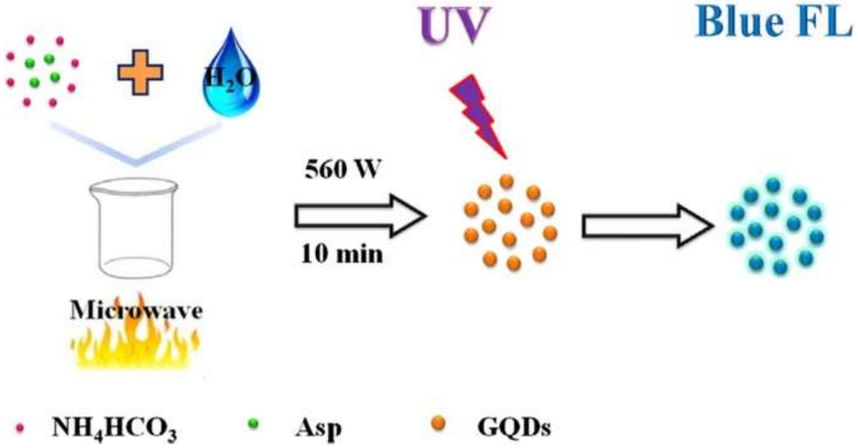


Figure - 1.14: Preparation Process of GQD by Microwave Method [30]

Top- Down Method

Hydrothermal Method:

The hydrothermal approach is a simple and quick way to make GQDs. Using a range of macromolecular or tiny molecular compounds as starting ingredients, GQDs can be produced at high temperatures and pressure. To make GQDs, high temperature and high pressure are used to disrupt the bonds between carbon components.

Electrochemical Oxidation:

In this particular process, carbon–carbon graphite bonds, graphene are oxidized and decomposed in high redox voltage circumstance (1.5-3 V) into making GQD.

Chemical Exfoliation:

It is one of the suitable methods for GQD synthesis. In this method c-c bonds of graphene, carbon nanotubes are destroyed by adding acids like H_2SO_4, HNO_3.Then it oxidises or exfoliates graphene in layers and GQDs are formed.

Bottom-up process

Electron-beam lithography:

Electron-beam lithography or EBL is a process of scanning a focused beam of electrons to draw custom shapes on a surface covered with an electron-sensitive film. It requires costly and professional equipment, by this method GQD can be synthesized even at room temperature. [21]

Microwave Method:

Because the hydrothermal method's long reaction time is a typical issue, microwave technology has evolved into a quick heating method that is widely employed in the fabrication of nanomaterial. It not only cut the reaction time in half, but it also boosted the yield. GQDs are purified by microwave irradiation utilising Asp (Aspartic acid), DI water and NH_4HCO_3. High fluorescence (blue) is observed in produced GQD.

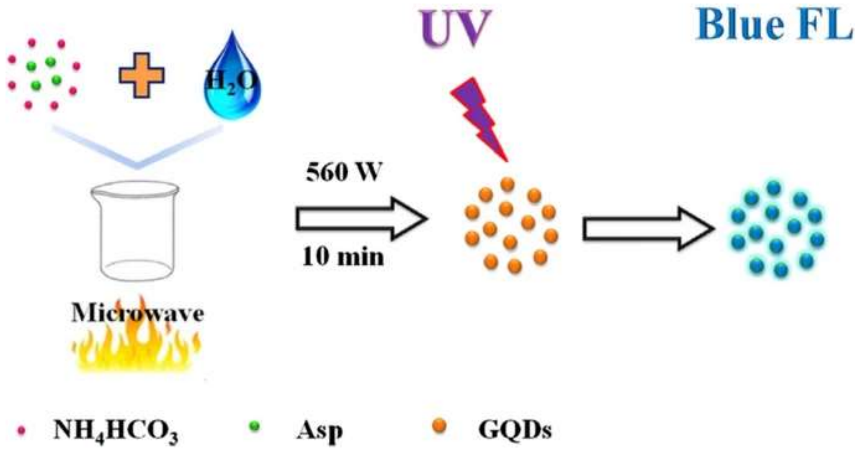
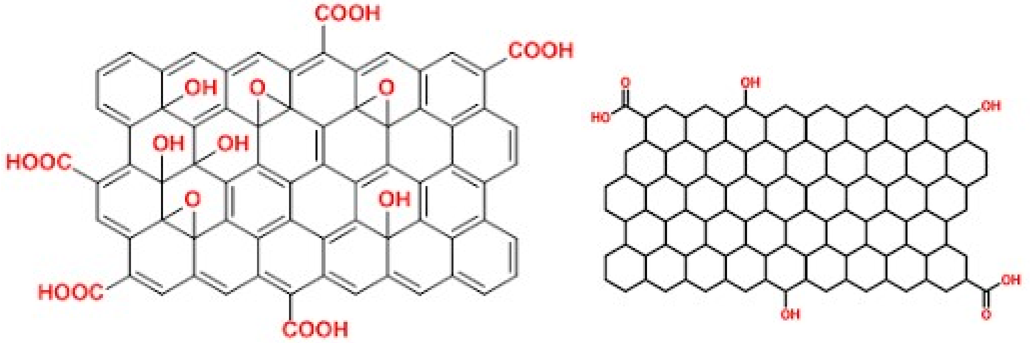


Figure 1.15: Preparation Process of GQD by Microwave Method [30]

1.4.4. Graphene oxide (GO) and Reduced Graphene oxide (RGO)

Graphene oxide (GO) and reduced graphene oxide (RGO) is an oxidized and redox compound of graphene respectively. GO has a strongly hydrophilic behaviour, which allows water molecules to penetrate between the graphene layers and thereby increase the interlayer distance even further. Introduction of strong acid and oxidizing reagents that creates oxygen functional groups on the surfaces and at the edges of the graphene layers giving rise to graphite oxide. In 1958 Hummers and Offeman reported the oxidation of graphite and the production of graphite oxide on immersing natural graphite in a mixture of H_2SO_4, $NaNO_3$, and $KMnO_4$.[22]



(a) (b)

Figure - 1.16: (a) Molecular Structure of GO (b) RGO

Graphene Oxide:

Graphene oxide (GO) can be synthesized from graphite oxide. The main difference between graphite oxide and GO is the interplanar spacing between the individual atomic layers of the compounds, which is caused by water intercalation. This increased spacing, caused by the oxidization process, sp^2 also disrupts the bonding network, meaning that both graphite oxide and GO are often described as electrical insulators. GO is a poor conductor but its treatment with light, heat, or chemical reduction can restore most properties of the famed pristine graphene. After fabrication of graphite oxide, GO can be obtained by exfoliating graphite oxide into monolayer sheets through a variety of thermal and mechanical methods. Among these methods thermal exfoliation becomes a popular method of GO exfoliation. Similarly, the mechanical method of exfoliation can be done by sonicating graphite oxide in water or polar organic media. Especially, sonicating and mechanical stirring can be combined together to exfoliate graphite oxide with a better efficiency than using any individual method. But the sonication has a great disadvantage that it causes substantial damage of GO platelets. It can reduce them in surface size from microns to nanometres. The first synthesis of GO is often attributed to Brodie, Staudenmaier, and Hummers and Offeman each of whom derived graphite oxide via the oxidation of graphite using various techniques. [22] Hummers and Offeman made a number of improvements on the original two techniques to make them safer, including the use of $KMnO_4$ as an oxidizer (rather than $KClO_3$, which evolves toxic ClO_2 gas) and the addition of sodium nitrate (to form nitric acid in situ rather than using nitric acid as a solvent). Due to the safer and more scalable nature of the Hummers' method, this is the one that is generally used (or, in most cases, slightly altered) to generate GO.

Reduced Graphene Oxide (RGO):

Reducing GO to produce RGO is an extremely vital process because it has a large impact on the quality of the RGO produced; therefore, it will determine how close RGO will come in terms of structure to pristine graphene. There are a number of ways reduction can be achieved, although they are all methods based on chemical, thermal, or electrochemical means.[23] Some of these techniques are able to produce very high-quality RGO, similar to pristine graphene, but they can be complex or time-consuming to perform. RGO produced by chemical reduction has relatively poor yields in terms of surface area and conductivity. Thermally reducing GO at temperatures of 1000 ^{0}C or more creates RGO that has been shown to have a very high surface area, close to that of pristine graphene. This thermal process damages the graphene platelet as pressure builds up, produces CO_2 and reduces mechanical strength by creating imperfections, vacancies etc. in its structure. Electrochemical reduction of GO produce high quality RGO, similar to the pristine graphene. Primary benefit of this process is that there are no hazardous chemical is used, so no toxic waste comes out.

Properties of GO and RGO:

i. GO is easily dispersible in water and organic solvents because of the presence of oxygen functionalities. This solubility of GO remains a very important property when it is mixed with other material to improve their conductivity.

ii. GO is often described as an electrical insulator because of the disruption of its sp^2 bonding networks. To recover, the reduction of GO yields RGO and hence electrical conductivity and honeycomb hexagonal lattice structure regained.

iii. Modified graphene can be achieved by functionalization of GO and chemical properties are changed. This makes it more adaptable for so many applications e.g. Optoelectronics, bio utilized devices, or importantly as a drug-delivery material.

1.4.5. GO & RGO Synthesis Methods

The discovery of GO & RGO brings new method of synthesis in light. Several methods are introduced through ages and in research papers. Synthesis of GO can be divided into two main categories- i) bottom-up methods where simple carbon molecules are used to construct pristine graphene; ii)top-down methods where layers of graphene derivatives are extracted graphite or other carbon source. The effective and useful methods are described here below-

Bottom-Up Methods

Chemical Vapour Deposition (CVD):

By this bottom-up method GO can be produced. In this process the substrate is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired thin film deposit. The waste gases pumped out from the reaction chamber. Here temperature is the vital physical quantity which is controllable. Depending, Requirement of precursors and the structure depends on the material quality. There are many various types of CVD processes like thermal, plasma enhanced (PECVD), hot wall etc. [24]

Silicon Carbide:

Silicon carbide (SiC) is one of the candidate materials for use in the first-wall and blanket component of fusion reactors, and is used in nuclear fuel particle coatings for high-temperature gas-cooled reactors. [25]

Top-Down Methods

The focus on top-down methods, which first generate GO and/or RGO are more popular for yielding graphene derivatives, in particular for use in nanocomposite materials.

Mechanical Exfoliation:

This is a top-down technique in nanotechnology, by which a longitudinal or transverse stress is created on the surface of the layered structure materials. Mechanical method of exfoliation can be done by sonicating graphite oxide in water or polar organic media. Especially, sonicating and mechanical stirring can be combined together to exfoliate graphite oxide with a better efficiency than using any individual method. But the sonication has a great disadvantage that it causes substantial damage of GO platelets.

Thermal Exfoliation:

During heating, the oxygen-containing functional groups attached on carbon plane decompose into gases such as H_2O, CO_2 and CO, which will diffuse along the lateral direction. This exfoliation occurs only if the decomposition rate of functional groups surpasses the diffusion rate of evolved gases. Here the interlayer pressure existing among adjacent layers is large enough to overcome their van der Waals interactions and pushes the layers separated from each other. Generally, a minimum temperature of 550 °C is necessary for the successful exfoliation at pressure [56].

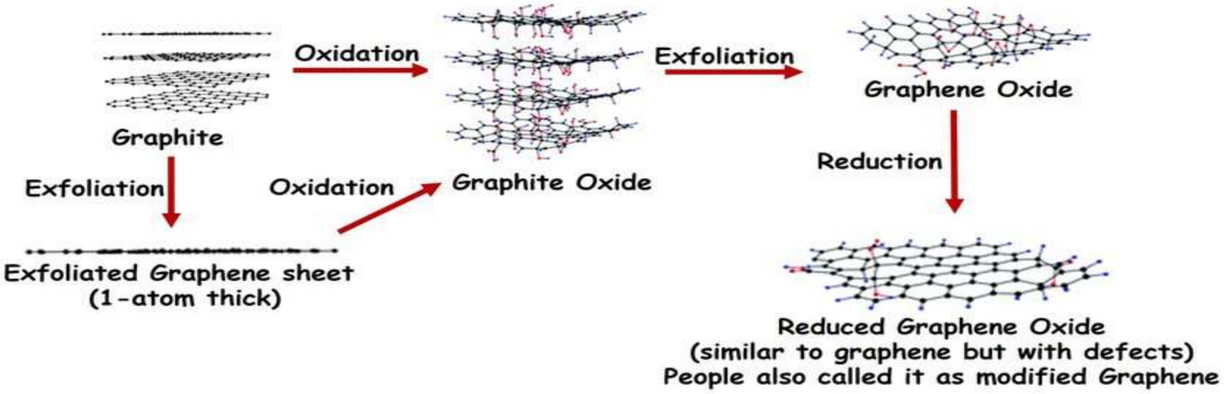


Figure - 1.17: Exfoliation of graphite oxide [58]

These two methods lack of quality and control. Due to that some other methods are introduced.

Modified Hummers Method:

Any method which changes or improves upon the synthesis route proposed by Hummers is regarded ubiquitously as a “modified Hummers method”.[27] In general, a carbon source (often graphite flakes or powders) is put into a protonated solvent (such as sulphuric acid, phosphoric acid, or some mixture of these) and a strong oxidizing agent (usually $KMnO_4$) is introduced. Following a dilution step, it is common to treat the resulting mixture with H_2O_2 to remove any metal ions from the oxidizer; this results in a yellow bubbling and ultimately a yellow-brown liquid. The resulting solids are then separated and treated with dilute hydrochloric acid to further remove any metal species, and the solution is washed and centrifuged several times with water until the pH of the solution is essentially neutral.

Tour Method:

GO (Graphene oxide) is prepared by mixing 90 mL concentrated H2SO4 (sulphuric acid) and 10 mL concentrated H3PO4 (Hydro-phosphoric acid). GO was reduced by using ascorbic acid as a reducing agent and distilled water. Then it is centrifuged and RGO is formed. This process involves several other similar or a little different steps. That is being discussed below:

(i) Oxidation or intercalation: GTO (graphite oxide) need to be prepared from graphite powder by mixing H_2SO_4 with potassium permanganate (strong oxidizing agent).

(ii) Exfoliation: Oxidized form of graphite should be dispersed into distilled water to form single-layer graphene oxide (GO). Then heating it with magnetic stirrer, black paste formed collected by filtration and followed centrifugation and drying a day at 60°C.

(iii) Reduction: In order to synthesize reduced graphene oxide (RGO), the GO was dispersed and ascorbic acid was added as the reducing agent, and same procedure followed. At Last, the black product should be washed with ethanol and distilled water, respectively. [28]

1.4.6. Applications of GQD, GO and RGO:

Biomedical Applications

- **Drug delivery system**

Drugs and various therapeutic agents are administered to treat specific diseases and disorders with the goal of achieving desired pharmacological effects with minimum side effects. The application of a controlled drug delivery system is a central strategy to enhance the therapeutic efficacy and safety of therapeutic molecules. The primary rationale of using a suitable drug delivery system is its ability to ensure a higher and longer duration of drug bioavailability and thereby enhanced therapeutic efficacy. Various materials with different structural forms are conjugated with drugs to prepare Nano drug delivery systems. Considering recent approaches, most commonly used drug delivery vehicles include nanoparticles (e.g., polymeric, ceramic, and metallic), liposomes, micelles, and dendrimers, etc. A substantial number of preclinical and clinical studies suggest their suitability for the treatment of various diseases. The number of materials for use in drug delivery applications is rapidly increasing, and such materials have shown great diagnostic and therapeutic potential [3]. Although liposomes have been used as potential carriers with unique advantages, including the protection of drugs from degradation, targeting and reduction of toxicity or side effects, their uses are limited due to inherent problems such as poor encapsulation efficiency, rapid leakage of the water-soluble drug in the presence of blood components and poor storage stability. On the other hand, polymeric nanoparticles offer certain specific advantages over liposomes. For example, they help increase drug/protein stability and have useful controlled release properties [4].

- **Bio imaging**

They are biocompatible and bio-toxic less, easy to synthesize, and have a wide range of emission wavelengths. They are also photo stable and water-soluble. These properties make them well-suited for bio imaging applications, such as imaging cells and tissues in vivo

- **Biosensor**.

Graphene quantum dots (GQD) possess a remarkable array of advantageous characteristics, making them highly sought-after for biosensor applications. These properties include exceptional solubility in water, making them easy to work with; their surface can be readily modified, and providing flexibility for various sensing strategies. Furthermore, GQD are non-toxic and exhibit multicolour emission, enabling diverse sensing capabilities. The exceptional biocompatibility of

GQD is crucial for their integration into biological systems. Their high cell permeability allows for efficient interaction with cellular components, facilitating precise and accurate detection.

Moreover, GQD demonstrate remarkable photostability, ensuring the durability of the biosensor over prolonged use. Due to these remarkable properties, GQD and graphene oxide (GO) biosensors are widely utilized for visual monitoring of various substances, such as glucose, phosphate, cellular copper, iron, and nucleic acids. These biosensors offer valuable insights into crucial biological processes and hold great promise for biomedical applications and disease diagnosis.

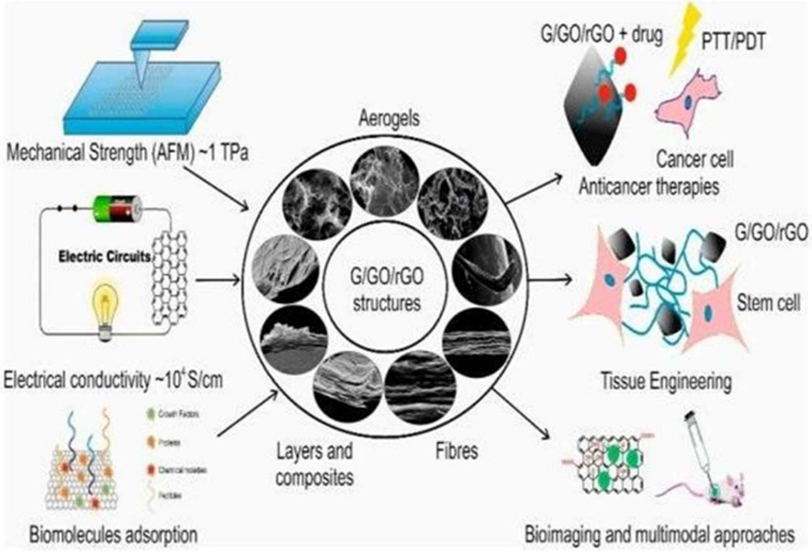


Figure - 1.18: Applications of GQD, GO [29]

Optoelectronics Applications

LED: Light Emitting Device:

GQD are great material for LEDs due to their stable light emitting, low cost and eco-friendliness. Nitrogen-rich GQD shows broad and bright visible light under UV illumination that would be worth utilizing in phosphor applications.

OSC: Organic Solar Cells:

By GQD organic solar cells can be made and this type of solar cell are very light weight, flexible and light harvesting capacity is high because it can absorb near infrared light. It has special optical properties to control efficiently by changing their quantum dot size [41]

Super capacitor:

GO & GQD can be electrode for super capacitors. These and some of its hybrid perform electrochemical performance achieved by efficient dispersion of reduced GO. It is useful in charge–discharge process and charge transportation [16].

DSC: Dye-Sensitized Solar Cells:

DSCs are very popular because the making process is very easy and the making cost is also very low. It is an organic dye, and the efficiency is also great. GO or GQD with stable light absorption made from broad and cheap sources show its potential in DSCs [41].

1.5 Aim of thesis

The primary aim of the present dissertation is to fabricate a new nanocomposite hybrid by combining the organic novel short-chain dyad (E)-(((9H-fluorene-2-yl)imino)methyl)-N,N dimethylaniline (NNDMBF) with graphene quantum dots (GQDs), graphene oxide (GO), and reduced graphene oxide (RGO) and finally the whole nanocomposite system has been incorporated within the chloroplast environment. Steady state and time-resolved spectroscopic techniques have been used to investigate the formations of charge-separated species and energy wasting charge recombination processes within the pristine dyad and its hybrid nanocomposite systems both without and with chloroplast. Theoretical predictions and NMR studies show that in the ground state, only the elongated (E-type) trans conformation of the pristine dyad exists. However, on photo excitation, these elongated conformers are converted into folded forms (Z-type) cis conformation. Time-resolved fluorescence spectroscopy (fluorescence lifetime by Time correlated single photon counting (TCSPC) method) measurements demonstrate that in acetonitrile medium and in the presence of GO and RGO nanoparticles, the organic-inorganic hybrid nanocomposite possesses a larger number of trans conformers relative to cis conformers, even in the excited singlet state. This indicates the possibility of slower energy-destructive charge recombination rates relative to the rates associated with charge separation within the dyad. In the present investigations, UV-Vis absorption, steady state and time resolved spectroscopic techniques by TCSPC have been used to investigate the same dyad when combined with GQDs/GO/RGO about the suitability of the nanocomposite forms in the designing of artificial light energy converters and compare it with the pristine form of the dyad NNDMBF. Finally, the results will be analysed to determine which form of the dyad is an effective energy storage candidate. This could lead to the development of a new, budget-friendly, and eco-friendly charge storage device (supercapacitor) or efficient energy storage device to help in solving the global energy crisis. By using steady state and fluorescence lifetime techniques it was observed that in the environment of chloroplast (**clp)** these nanocomposites somewhat suffer lacking in the retention capability of trans-form (elongated structure) in the excited state increasing the possibility of occurrences of energy wasting charge recombination process due to predominance of folded (cis) form. Detailed time resolved spectroscopic measurements were made to compare the efficiency of light energy conversion of the pristine dyad and when it adsorbs the nanosurfaces of CQD, GO and RGO ie., of the same dyad in nanocomposite forms and finally when the nanocomposites are incorporated in **clp** environment. Our main interest is to see how highly efficient nanocomposite devices behave when bathed under the environment of chloroplast. The results are described in the present thesis.

1.6 Literature Review

NNDMBF– short-chain synthesized dyad has suitability in so many fields. As a candidate in LEDs, solar cells, data storage and also it has the potential to serve as better candidate for artificial light energy conversion systems relative to its pristine form. From the present time resolved spectroscopic results it could be hinted that relatively stable trans-conformer in the excited state in case of the nanocomposite system of dyad NNDMBF-GO (or RGO or GQD) in comparison to the pristine form may arise from the surface trap effects. In future it may able to solve the global energy crisis phenomenon.

T. Ganguly*et al*. [19] studied the photophysical properties and the nature of the photoinduced electron transfer (PET) reactions within a synthesized anisole (A)-thioindoxyl (T) dyadsystem (24MBTO) by using electrochemical, steady state, and time-resolved spectroscopic techniques. The results demonstrate the formations of the two types of isomeric species: Z- and E- forms, resulted from the charge separation reactions. From the detailed studies it reveals that the present thioaurone may behave as a versatile photoswitchable system.

Wang *et al.* [20] reported that optimization of photophysical process, such as light absorption charge separation and introduction of novel photophysical phenomena. The application of basic principles for solar to chemical energy conversion are also reviewed. The localized temperature increase by the nanoparticles will increase with the intensity of the incident light and elevated temperature. The efficient sunlight harvesting and e^-/h^+ excitation of semiconductors and the selective organic synthesis and self-replication of bio system. This amenable route by bridging the natural and artificial systems bring great efficient and sustainable solar-to-chemical energy conversion.

T Ganguly *et al*. [21] reveals from steady state and fluorescence lifetime measurements that due to photoexcitation of benzotriazole (BZ) part of the bichromophore, 9(1-H-benzotriazole-lylmethyl)-9H-carbazole (BHC), singlet–singlet energy transfer takes place to populate the lowest excited singlet of carbazole (CZ). CZ, thus being excited indirectly via energy transfer process, undergoes strong charge transfer (CT) reaction with the surrounding polar medium acetonitrile (ACN). On the other hand, very weak CT band was apparent when CZ part, within BHC, was directly excited. In less polar tetrahydrofuran (THF) and polar benzonitrile (BN) environment, lack of formation of CT band strongly suggests in favour of the electron-accepting behaviour of ACN. Moreover, by measuring the emission spectra of BHC in micro crystals and of 30 bilayers mixed LB film at high mole fraction of BHC molecules, the possibility of excimer formation or aggregation has been ruled out. Thus, BHC, when dissolved in ACN, acts as a triad system of BZ–CZ–ACN where BZ acts as an antenna molecule and CZ as a reaction centre. The possible role of the bichromophoric system BHC as an artificial photosynthetic or solar energy conversion device has been hinted. Chakraborty *et al.* [22] reported that the core-shell nanostructures have generally found to be improved properties thus the light energy conversion device developed which is more efficient by using chore-shell nanocomposites without using only nanoparticles.

T. Asahi *et al*. [23] investigated photoindused intramolecular charge separation (CS) and charge recombination (CR) of the product ion pair (IP) state of a series of fixed-distance dyads consisting of free-base porphyrin or zinc porphyrin and quinines by using femtosecond laser spectroscopy, to determine energy gap and temperature dependences of CS and CR reactions in nonpolar media. Obtained CS rates were in the normal region and CR rates were in the inverted region. They have confirmed that the activation barrier for the CS reaction increases with a decrease of the energy gap, while the CR process is activation less, indicating the dominant effect of the high-frequency quantum mode in the inverted region. They also examined solvent polarity effect upon the energy gap dependence upon CS rate constant and CR rate constant. Here solvent reorganization energy increases with the solvent polarity, with the CS rate constant but CR rate constant shows little solvent polarity dependence.

T. Ganguly *et al*.[24] observed the photophysical properties of the synthesized short-chain organic dyad, 1-(4-chlorophenyl)-3-(4-methoxy-naphthalen-1-yl)-propenone (MNCA) in isotropic media and gel (P123) environment by using steady state, time-resolved spectroscopic techniques and fluorescence anisotropy decay. From the NMR and time-resolved spectroscopic studies E-isomeric form (elongated nature) of the charge-transfer species of the dyad MNCA appears to be the only isomeric form in the ground state and this conformation retains even after photo excitation whatever be the nature of the environment, the isotropic solution or micro-heterogeneous medium (gel phase of P123).

T. Ganguly *et al.* [25] studied with the help of electrochemical, steady state and time resolved fluorescence (fluorescence lifetimes by using time correlated single photon counting technique) and nanosecond laser flash photolysis methods, the nature of charge separation along with the energy wasting charge recombination processes within a short-chained organic dyad 1-(4-bromo-phenyl)-3-(2-methoxynapthalen-1-yl)-propenone (MNBA) has been revealed. In MNBA, the donor 2-methoxynapthalen (2MNT) is connected with the acceptor p-bromoacetophenone (PBA) by an unsaturated olefinic bond. Though in the ground state elongated type structure (E-form) is observable from NMR spectra but on photoexcitation, another conformers possibly of the nature of folded type isomeric species (Z-form) were also apparent from time resolved fluorescence measurements. However preponderance of elongated form in the excited singlet state has been established from this time resolved measurement. The energy wasting charge recombination rate is determined from the transient absorption measurement by nano second laser flash photolysis technique, was found to be significantly lower than the charge separation rate, which is measured from time resolved fluorescence. This observation demonstrates that MNBA may serve as an efficient candidate to construct artificial light energy conversion device or components of molecular photovoltaic cells.

T. Torres *et al.* [26] investigated the photophysical properties of new dyad molecule, which is composed of a covalently linked Zn-phthalocyanine (donor) and a C_{60} derivative (acceptor). They presented an experimental evidence of long lived charge separation in solid state with a life time several order higher than in solution. It is the basis of possible photovoltaic application.

T. Ganguly*et al.* [27] were made steady state and time resolved spectroscopic measurements at the ambient temperature on an organic dyad, 1-(4-Chloro-phenyl)-3-(4-methoxy-naphthalen-1-yl)-propenone (MNCA), where the donor 1-methoxynaphthalene (1 MNT) is connected with the acceptor p-chloroacetophenone (PCA) by an unsaturated olefinic bond, in presence of Ag@TiO_2 nanoparticles. Time resolved fluorescence and absorption measurements reveal that the rate parameters associated with charge separation within the dyad increases whereas charge recombination rate reduces significantly when the surrounding medium is changed from only chloroform to mixture of chloroform and Ag@TiO_2 (noble metal-semiconductor) nanocomposites. The observed results indicate that the dyad being combined with core–shell nanocomposites may form organic– inorganic nanocomposite system useful for developing light energy conversion devices.

T. Ganguly *et al.* [28] observed that various photophysical properties were measured by using UV-vis absorption, steady state and time resolved spectroscopic experiment. Both the silver (Ag)-dyad MNTMA and gold (Au)-MNTMA hybrid nanocomposites system result were compared and a remarkable variation have been observed between the two nanocomposites.

T. Ganguly *et al.* [29] measured different photophysical properties of silver (Ag)-dyad MNTMA system by using UV-vis, steady state and time resolved spectroscopic technique and the observed result is compared with the gold (Au)-MNTMA hybrid nanomaterials. Considerable enhancement of the plasmonic absorption band observed in the case of Ag-dyad system, which is absent in case of the other Au-dyad nanocomposite system. From the measured fluorescence lifetime values, preponderance of folded conformation which facilitates charge recombination was observed even in the excited state in the case of Ag-dyad hybrid nanocomposite system unlike the situation observed for Au-dyad hybrid nanocomposite where elongated conformations were found to prevail significantly on photo excitation. Transient absorption measurements by laser flash photolysis method state that energy destruction rate is much faster in case of Ag-dyad system relative to the Au-dyad nanocomposite device.

Bhattacharya *et al.* [30] reported that nature of charge separation and recombination process within an organic dyad having short spacer. By this investigation it revealed that by 1-(4-Bromo-phenyl)-3-(2-methoxy-naphthalen-1-yl) - propenone (MNBA) candidate an efficient light energy conversion device can be constructed. So, by this system in future low cost-efficient energy conversion device can be made.

Bhattacharya *et al.* [31] investigate that charge recombination process in light energy conversion device can newly modulated by using metal-semiconductor nanoparticles. By using of TiO_2 nanoparticles it observed that it is inferred so, much improved version of light energy conversion device. In this system charge separated species could be protected for long time period.

T. Ganguly *et al.* [32] examined from Ultraviolet-visible absorption, steady state and time resolved spectroscopic investigations on the pristine dyad, dyad-spherical gold nanoparticles (GNP) and dyad-star shaped gold nanoparticles (GNS). It was observed that though in the ground state pristine form of dyad possesses trans- (elongated and planar) isomer but on photo excitation trans- converts into cis-structure (folded). Interestingly, the dyad exhibits different behaviour when it combines with GNP or GNS. In nanocomposite form, even on photo excitation some ground state trans-structure still retains its identity in the excited state. The 60% of the trans-species remains unchanged in the excited state due to excitation of dyad-GNS system and possibly this configuration facilitates the hindrance of energy destructive charge recombination processes. The dyad-GNS nanocomposite appears better light energy storage device than dyad-GNP and the pristine form of the dyad in present investigation.

Mitra *et al.* [33] observed that the effect of carbon quantum dots (CQD) with short chain dyad and its energy storage capacity. By time resolved spectroscopic technique the investigations performed on pristine short chain dyad, (E)-4-(((9H-fluorene-2-yl)imino)methyl)-N,Ndimethylaniline (NNDMBF) and its nanocomposite forms with CQD or NCQD. The experiment result shows that more than 80% trans structure of ground state dyad could be protected in the environment of CQD even on photo excitation and it perform as a great energy storage capacity.

Gust *et al.* [34] reported that complicacy of natural photosynthesis can be reduced by biomimic system. The sunlight converted into chemical energy by the liposomal device which is a biometric nanoscale machine. The efficiency of the system is very high. The overall energy transduction process in the liposomal system mimics the solar energy conversion system of a photosynthetic bacterium.

Rozzi *et al.* [35] observed that the fundamental challenge is how efficiently light energy converted into electricity or chemical fuels. In artificial photosynthesis and photovoltaic device, this conversion is generally thought to happen on ultrafast, femto-to-pico second time scales. Primary charge transfer process in a supramolecular triad, a prototypical artificial reaction centre also investigated by them.

Sen et al. [36] reported that the surface energy transfer between confined dye and Au nanoparticles has been studied by time resolved and steady state spectroscopy. After analysis it reveals that the energy transfer form dye to Au nanoparticles is a surface energy transfer process. Such energy transfer between confined dye and Au nanoparticles could be the new way to designing new light harvesting system.

Dutta *et al.* [37] observed that a common process for storage of energy involves the photo excitation of a donor molecule followed by electron transfer to an accepter. They trap the photo sensitizer donor, trisbipyridine ruthenium (II), in the super cages of zeolite.

Zhang *et al.* [38] reported that nanostructured materials have various advantages like huge surface to volume ratios, favourable transport properties, altered physical properties and confinement effect resulting from the Nano scale dimension. So, it has a huge application such as solar cells, catalysts, thermoelectric, lithium-ion batteries, super capacitors etc. By this review some applications are benefited like providing a large surface area to boost electrochemical reaction, generating optical effects to improve optical absorption of solar cells.

Balaya *et al.* [39] discussed that novel concept at nano size for the development of excellent material which achieve efficient energy conversion and storage. Efficient waste heat conversion by thermoelectric device using nanostructured materials is highlighted. He reported that the performance of super capacitors can be enhanced by nano sized metal oxides.

Edward *et al.* [40] discussed that the uses and application of hydrogen and fuel cells. Hydrogen and fuel cells can be used in transportation, distributed heat and power generation, and energy storage systems. Fuel cells converted into hydrogen or a hydrogen-rich fuel and an oxidant directly into electricity using. It is a low temperature electrochemical process. In future it has a bright scope because it is sustainable energy with low CO_2 emission.

Brudving *et al.* [41] reported that fossil fuel dependency has various drawbacks like energy security issues and greenhouse gas emissions. It could be avoided by fuel producing artificial system that mimic natural photosynthesis, directly converting solar energy into fuel. They reviewed three main point of photosynthesis, light harvesting, charge separation and catalysis. The design of dye-sensitized solar cells for fuel generation is discussed here.

Eustis *et al.* [42] reviewed that noble metal nanoparticles and their current application they discussed about noble metal surface plasmon resonance and their radiative and non-radiative properties of nanocrystal different shapes. By changing the size or shape of nanoparticles the properties also change. By applying these new applications could be developed in future.

T. Ganguly *et al.* [43] observed the photo switchable characteristics of 1-(4- chloro-phenyl)-3-(1-methoxy-3,4-dihydro-naphthalen-2-yl) propenone (MNCADH) which is a novel self-synthesized dyad. They reported in ground state of this dyad found as ‘trans’ isomer. By steady state and time resolved spectroscopy technique it seen that both ‘cis’ and ‘trans’ isomers are present in the excited state. In excited state it is found that trans–cis interconversion energy barrier becomes lower than ground state and in the excited state trans–cis conversion occurs more efficiently.

Mandal *et al.* [45] reported that synthesis and characterization method of a novel organic dyad, 3-(1-Methoxy-3,4-dihydro-naphthalyn-2-yl-)-1-p-chlorophenyl propanone. They fabricate new hybrid nanocomposites by combining the organic dyad with different noble metals, semiconductor nanoparticle and noble metal-semiconductor core/shell nanocomposites.

Paul *et al.* [46] observed that from the UV-vis, steady state and time resolved spectroscopic investigations on the pristine dyad, dyad-spherical gold nanoparticles (GNP) and dyad-star shaped gold nanoparticles (GNS), in the ground state the dyad in its pristine form possesses trans-type isomer but on photo excitation trans-form converts into cis-structure. The dyad performs different behaviour when it combines with GNP or GNS. The dyad-GNS nanocomposite perform to be the best possible light energy conversion or storage device.

Olabi *et al.* [47] reviewed that in most of the energy storage device application graphene perform outstanding performance. Graphene is capable to enhance the performance, the durability of graphene also great. In this investigation the application of graphene in energy storage device, absorbance and electrochemical sensors highlighted.

Park *et al.* [48] investigated that graphene in micro-scale devices to take its full advantages, it is important to integrate two-dimensional graphene nanosheet into a micro/macro sized structured that can fully utilize graphene’s nanoscale characteristics. For this a novel spray assisted self-assembly process to create a spherically integrated graphene microstructure using high temperature organic solvent.

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Chapter: 2

Materials and Experimental Methodology

- ❖Materials
- ❖Experimental Methodology
- ❖References

2.1. Materials

The spectroscopic grade solvents acetonitrile (ACN) (SRL) and cyclohexane (CH) are purified using normal processes, and then tested before use for the absence of any impurity emission in the wavelength range of interest. Water is deionized using the Millipore and Milli-Q systems. The primary experimental solutions were made by dissolving the necessary amount of dyad, CAN, and CH.

2.1.1. Synthesis and Characterization of the Novel short-chain dyad (NNDMBF)

Figure 2.1 depicts the investigated dyad synthesis technique. 2-amino fluorene was produced during the method. In a round bottle flask, 7 mL of anhydrous ethanol was added to a combination of 1.5 mmol 2- aminofluorene and 1.5 mmol 4-(dimethylamino) benzaldehyde. The reaction mixture was stirred for 2 hours at room temperature. The solvent was removed under high vacuum after the reaction was completed (monitored by thin layer chromatography, TLC), and the crude reaction mass was washed several times with hexane to obtain the pure product, which is the dyad €-4-((9H-fluorene-2-yl)imino)methyl)-N,N-dimethylaniline (Compound 5)[1].

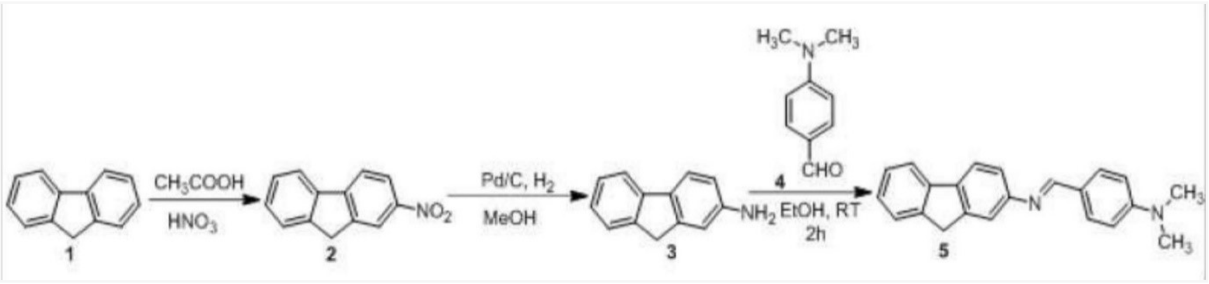

Figure 2.1: Synthesis procedure of NNDMBF dyad. [1]

On a Bruker AVIII- 500, 1H and 13C NMR spectra (Figures 2.2-2.3.) were acquired. Chemical changes were measured in parts per million (ppm). In Hertz, coupling constants (J values) were reported. The chemical shifts of 1H NMR were compared to CDCl3. The chemical shifts of 13C NMR were compared to CDCl3.

Value: ^{1}H NMR (500MHz, CDCl3): δ =2.90 (s, 6H), 3.81 (s, 2H), 6.62 (d, 2H, J = 8.5Hz), 7.13-7.18 (m, 2H), 7.24-7.28 (m, 2H), 7.41 (d, 1H, J = 7.5 Hz), 7.64-7.69 (m, 4H), 8.31 (s, 1H). ^{13}C

NMR (125 MHz, CDCl3): δ = 36.9, 40.2, 111.6, 117.5, 119.5, 120.2, 120.3, 124.5, 125.0, 126.2, 126.8, 130.4, 138.9, 141.6, 144.4, 151.9, 152.4, 159.6[1]

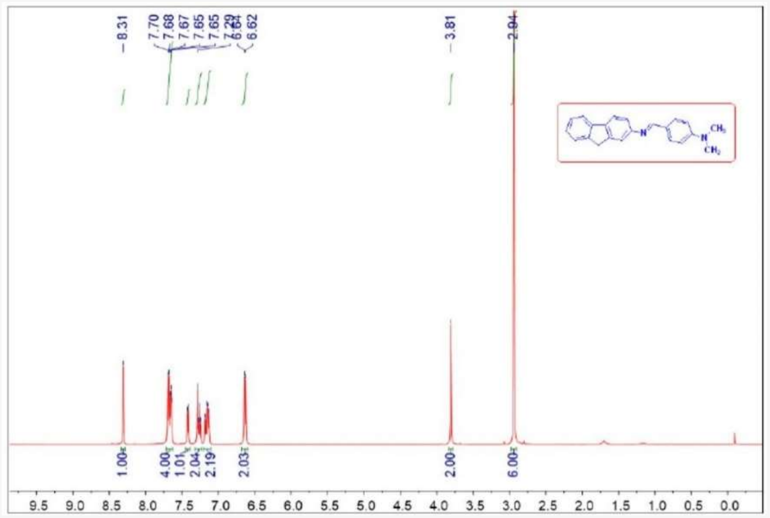

Figure - 2.2: ^{1}H NMR of (E)-4-(((9H-fluorene-2-yl)imino)methyl)-N,N-dimethylaniline[1]

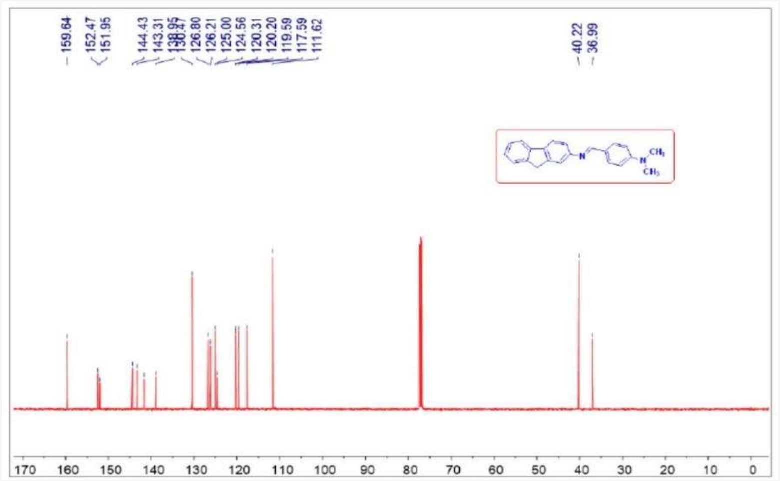

Figure - 2.3:^{13}C NMR of (E)-4-(((9H-fluorene-2-yl)imino)methyl)-N,N dimethylaniline[1]

The astounding possibility of two conformers: Trans and Cis (Figure 2.4) of our dyad can be inferred from the molecular structure of the dyad. Because the N atom has no proton, coupling constant values from NMR cannot be used to forecast the dyad's potential ground state conformation. Theoretical simulations on the ground state optimal geometry of the dyad

NNDMBF utilising the BL-LYP/6- 311g (d,p) level of theory on HOMO–LUMO surfaces.reveal that there may be two types of conformers, Cis- and Trans-, with the latter being more stable in the ground state. As a result of the preceding theoretical expectations, both cis and trans forms of the dyad exist in the ground state, with the latter predominating [1].

Figure - 2.4: Trans& Cis conformers of dyad [1]

The electron donor 4(N,N-dimethylamine)benzaldehyde (NNDMB) is coupled to the acceptor fluorene(F)[1] by a short chain in a novel short-chain dyad (NNDMBF) (Figure 2.5).

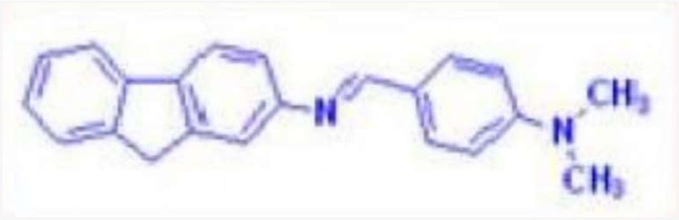

Figure - 2.5: Novel short-chain dyad (NNDMBF) [1]

2.1.2. Graphene Quantum Dots (GQD) Synthesis

Citric acid is pyrolyzed to make graphene quantum dots (GQD) after heating and melting five grams of citric acid, it turned a dark orange colour in 25–30 minutes. At room temperature, a 1.5 M solution of NaOH was added drop wise to a melting thick solution of citric acid. [2]

2.1.3. Graphene oxide (GO) and Reduced Graphene oxide (RGO) Synthesis

GO Synthesis:

GO can be produced using a modified Hummer's method. [3] In this process, 2gm of graphite powder was combined with 1 gm of $NaNO_3$ in an ice bath. Now, 130 mL of concentrated H_2SO_4 was added to the mixture while swirling it. 6 gm of $KMnO_4$ was gently added under vigorous stirring conditions, keeping the reaction temperature of the mixture around 200 C. The reaction temperature was gradually increased to 400 C, and the mixture was stirred for 6 hours. The colour of the combination shifts from dark grey to greyish green at this point. An additional 6 gm of $KMnO_4$ were added to the mixture and stirred for another 6 h so that the color of the mixture becomes greyish brown. Now, 250 ml of triple distilled water was slowly added to the solution which raises the temperature of the solution to around 960 C at which the mixture was stirred for 30 min. The solution was then cooled down to room temperature. Now, an additional 500 ml triple distilled water and 15 ml 30% H_2O_2 were added to the solution to stop the oxidation. At this stage, the color of the solution becomes yellow ochre signifying the high oxidation level of graphite.

Now, the yellow solution was washed two times with 1M HCl (Hydrochloric Acid) solution and repeated washing was done with triple distilled water until a pH of 5 was obtained. This was done by centrifugation of the solution and decantation of the supernatant. A rigorous washing and decantation step is necessary to exfoliate the graphene oxide layers and to remove the unexfoliated graphene oxide layers. The thick yellow brown gel was filtered and dried overnight to get a fine yellow graphene oxide (GO) powder. A stoichiometric amount of GO was then taken in triple distilled water and ultrasonicated for 30 min to get a homogeneous solution.

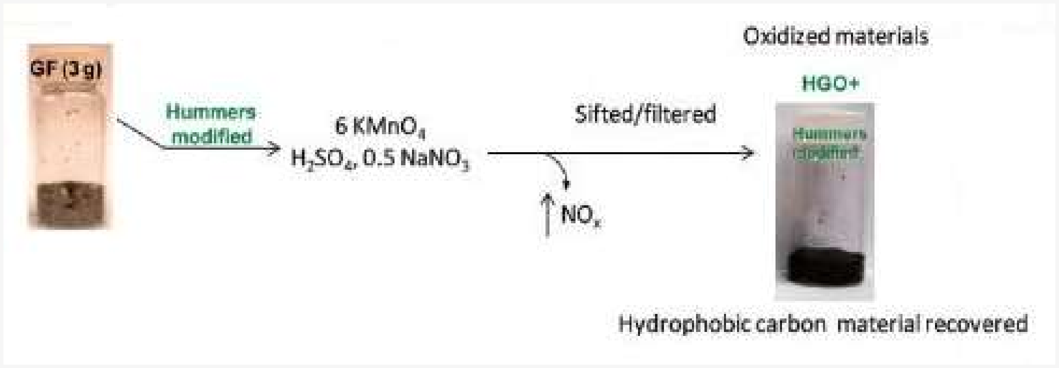

Figure - 2.6: GO Synthesis process [3]

RGO Synthesis: Oxidised material samples were reduced with hydrazine hydrate before being annealed in Ar/H_2 at 300 and 900 degrees Celsius. 100 mg of enhanced GO materials are distributed in 100 ml distilled water and agitated for 30 minutes to reduce hydrazine. 1 mL hydrazine hydrate is then added. After 45 minutes of heating at 950°C in a water bath, a black solid precipitated from the reaction mixture. Filtration isolates the products, which are then washed with distilled water to yield 54 mg of chemically reduced enhanced GO i.e. RGO. NMR spectra show no signal from oxidised carbon after reduction. This signifies that RGO is of very high grade. We estimate that individual RGO flacks have a thickness ranging 1-3 nm based on AFM measurements [3].

Structural characterization of GO and RGO:

In our experiment we used GO where the level spacing is around 9.0 Å (from XRD spectra). The X-ray photoelectron spectroscopy (XPS) confirms that GO produced by modified Hammer's method is more oxidized than GO produced by Hummer's methods. XPS confirms that improved GO has 63% oxidized carbon and 37% graphitic carbon. From 13C NMR we get the apparent peak of oxidized carbon of GO at around 287 eV. TEM images confirms the structure regularity of GO. UV-Vis spectra supports the regular structure of GO is due to greater retention of carbon ring in basal plane. Large extinction coefficient of GO indicate that it has large number of aromatic ring or isolated aromatic domain.

Although the following λ_{max} results from the electronic transition show that these aromatic rings are not extended conjugation, total absorption indicates that GO produced by the modified Hummer's approach retains more aromatic rings than GO produced by Hummer's method [3].

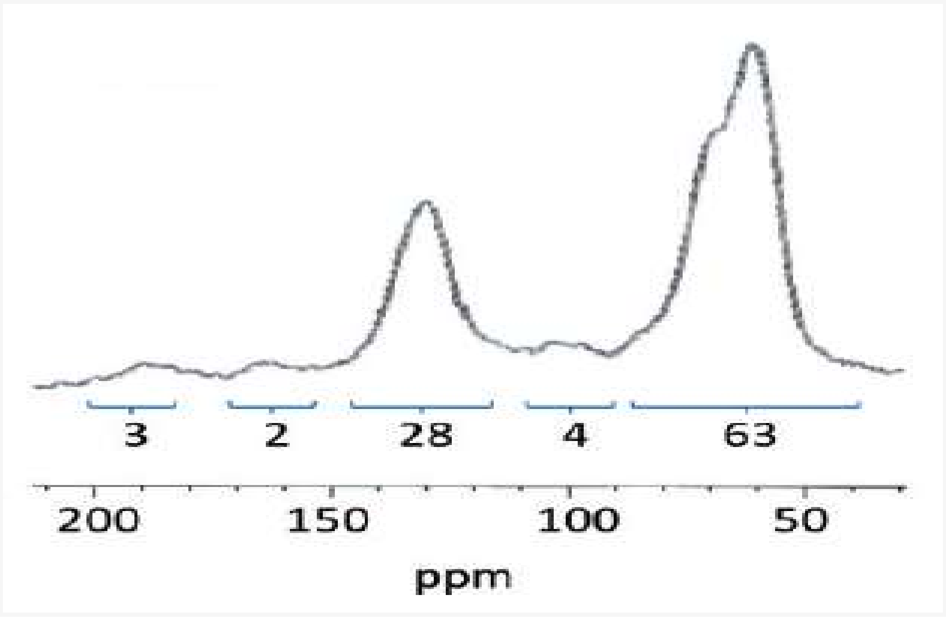

Figure - 2.7: 13C NMR Spectra of GO [3]

Isolation of Chloroplast (clp):

Young and fully expanded deveined mung bean leaves were ground with a blender in a medium containing mannitol, HEPES, EDTA, $MgCl_2$ and BSA in ice cold conditions. In brief, the leaves were homogenized in a chloroplast isolation buffer containing 330 MM mannitol, 30 MM HEPES, 2 MM EDTA, 3 MM $MgCl_2$ and 0.1 % w/v BSA (pH 7.8) using a blender for 15s. The slurry was filtered through 8-layers of cheese cloth followed by centrifugation at 250 g for 5 min. The supernatant was again centrifuged at 1000g for another 5min. The chloroplast was washed and resuspended in an extraction buffer and used for tracking the photosynthetic pathway.

2.2 Experimental Methodology

2.2.1. High resolution transmission electron microscope (HRTEM)

It's a type of transmission electron microscopy with a modern twist (TEM). For high magnification of nanomaterials, HRTEM is utilised. HRTEM is an excellent imaging technique for nanomaterials at the atomic scale because of its high resolution. The TEM is a technique that gives morphological, compositional, and crystallographic information by using energetic electron contact with the material. HRTEM creates an interference image by using both transmitted and scattered electrons. It's a phase contrast image that can be as small as a crystal's unit cell. HRTEM has been utilised extensively and successfully for investigating crystal structures and lattice defects in a variety of sophisticated materials at the atomic level.

Point defects, stacking faults, dislocations, precipitates grain boundaries, and surface features can all be characterised with it. HRTEM has a 2D spatial resolution of around 0.05 nm. In 3D crystal, different views from various angles are combined to create a 3D map. Electron crystallography is the name for this method.

Working principle:

TEM i.e. Transmission electron microscope has three important sections:

1. Depending on the application, the specimen system can be stationary or move slowly. The mechanical stability of the TEM plays an essential role in defining its resolution.

2. The illumination system is made up of an electron cannon and two or more condenser lenses that focus the electron beam on the sample. The diameter of the beam is determined by the specimen arrangement.
3. At least three lenses are used in the imaging system to provide a magnified image of the sample on a fluorescent screen or a monitor of an electronic camera system. The unique resolution of the microscope is determined by the imaging lens design.
4. Image recording device e.g. CCD with photodiodes is used to record the image produced.

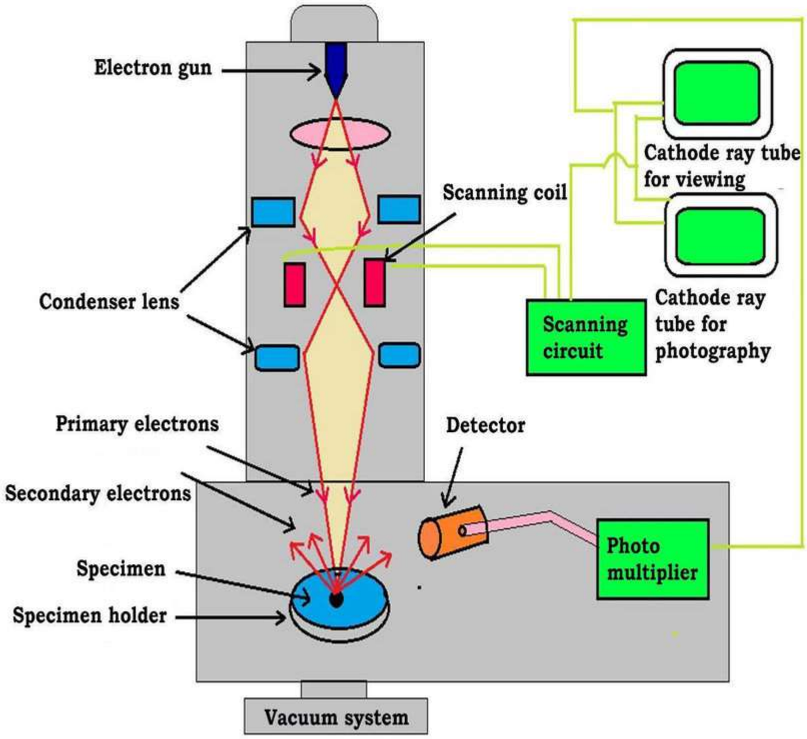

Figure - 2.8: Schematic diagram of HRTEM [19]

Components:

- **Specimen system**

Because any drift or vibration would be amplified in the final image, the specimen stage is designed to keep the specimen as still as possible. TEM specimens are always round, having a 3 mm diameter. The specimen must be perpendicular to this disc and thin enough to let electrons to pass through and generate the magnified image. The specimen is first placed in a container that can be evacuated before entering the TEM column. The specimen stage is divided into two types: side-entry and top-entry. The specimen is attached to the end of a rod-shaped specimen holder and inserted horizontally through the airlock, which is then triggered by rotating the specimen holder around its long axis. The specimen is clamped to the bottom end of a cylindrical holder with a conical collar in the top-entry stage. A sliding and tilting arm loads the holder into position through an airlock, which is subsequently removed and retracted. The cone of the specimen holder fits snugly into a conical well of the specimen stage inside the TEM, which may be manipulated in the horizontal (x and y) directions by a precision gear system.

- **Illumination system**

The energy of the electron beam produced by the electron cannon is adequate to pass through the sample specimen. An electron source, a cathode (due to the high negative potential), and an electron-accelerating chamber make up this cannon. The electrons are emitted through a process known as thermo-ionic emission. A V-shaped filament composed of tungsten wire is spot-welded to straight-wire leads that are installed in a ceramic or glass socket as the electron source. The filament is heated to roughly 2700 K using a direct current (dc), at which point tungsten emits electrons into the surrounding vacuum. The electron gun's filament can be constructed of tungsten or lanthanum hexaboride (LaB6). Although LaB6 source is more expensive than tungsten filament, it has a longer lifespan. The filament is encircled by a control grid with a central aperture positioned on the column's axis; the cathode's apex is positioned at or slightly above or below this aperture. The cathode and control grid are insulated from the rest of the instrument and have a negative potential equal to the required accelerating voltage.

With the help of an electric field parallel to the optic axis, electrons are accelerated to their final kinetic energy E_0 after emission from the cathode. A potential difference V0 between the cathode and anode is used to create this field. An anode is a circular metal plate with a central hole through which an accelerated electron beam emerges [6].Pass through the middle aperture at a constant energy if the high voltage has stabilised sufficiently. The electron gun's control and alignment are vital to its successful operation.

The condenser lens must have at least two electron lenses in order to provide a high-quality magnified image of the sample. A powerful magnetic lens is used as the first condenser lens. It creates a real image by using a virtual electron source. The spot size can be used to adjust the lens current. The weak magnetic lens used as the second condenser lens yields little or no magnification. This lens has a condenser aperture with a variable diameter that allows the angle of illumination of the electron form optic axis to be altered. The use of a small spot size reduces the effects of heating and irradiation on the specimen. In order to move the electron beam (incident on the specimen) in the y and x directions, the illumination system includes two pairs of coils that apply homogeneous magnetic fields in the horizontal (x and y) directions. A second set of coils is used to alter the incident beam's angle with respect to the optic axis.

- **Image producing system**

On the viewing screen or on the digital display system, the TEM imaging system creates a magnified image of the specimen. The quality and design of these lenses, particularly the first imaging lens, the objective lens, have a significant impact on the image's spatial resolution. With a short focal length, it's a powerful lens. To avoid picture drift caused by thermal fluctuations, this lens must be kept at room temperature. The TEM also contains precision controls that allow the specimen picture to be accurately focused on the viewing screen by making small fractional adjustments to the objective current. The first condenser lens has a great deal of focusing power. The second condenser lens creates a nearly parallel beam for analytical electron microscopy.

We can restrict electrons to arrive at the specimen parallel to the axis and must remain unscattered during their passage through the specimen using parallel lighting and properly controlled tilt controls. When an electron is scattered by one or more atoms in the material, it returns to the optic axis at the same angle. The diaphragm around the aperture absorbs electrons scattered at larger angles, so they don't contribute to the final image. We can assure that practically all scattered electrons are absorbed by the diaphragm by reducing the deflection angle. As a result, parts of the material that scatter electrons strongly appear as dark areas in the final image, which is referred to as diffraction contrast. Using an objective stigmator positioned below the objective lens, the TEM operator can eliminate blurring and correct for axial astigmatism in the objective. A diaphragm, which limits the specimen region from which electron diffraction is recorded, can also be used here. Only electrons that fall within the aperture's diameter are transmitted through it. As a result, the diaphragm's introduction offers diffraction data with good spatial and angular resolution.

Between the objective and the final lens in a TEM system, there are numerous lenses. This intermediate lens is primarily used for two purposes. First, image magnification can be altered in small steps by altering the focal length, which is commonly 103-106. Second, an electron diffraction pattern can be formed on the TEM viewing screen by increasing the intermediate lens excitation. A projector lens is then used to create an image or diffraction pattern across the entire TEM screen. The final-image magnification is the algebraic product of each imaging lens' magnification factors.

- **Image Recording**

The electron picture is monochromatic and must be made visible to the naked eye either by letting electrons to fall on a fluorescent screen at the foot of the microscope column or by digitally recording the image for display on a computer monitor. Computerized photographs are saved in TIFF or JPEG formats and can be examined or image-processed before being published. Charged coupled diode (CCD) sensors with a million photodiode array are used in this electronic image recording. There are various advantages to using electronic recording. The recorded image may be seen on a display screen at a high magnification, which makes focusing and astigmatism correction much easier. The image data is saved digitally in computer memory before being transferred to magnetic or optical discs, where prior photographs can be quickly accessed for comparison. The image's digital nature also allows for numerous types of image processing.

2.2.2. Ultraviolet–Visible Spectroscopy

Introduction

UV–Vis Spectroscopy, sometimes known as UV–Vis Spectroscopy, is a technique for measuring light absorbance in the ultraviolet and visible portions of the electromagnetic spectrum. It makes use of visible and near-infrared light. Incident light can be absorbed, reflected, or transmitted as it strikes materials. Atomic excitation is caused by the absorption of UV-Vis radiation, which refers to the transition of molecules from a low-energy ground state to an excited state [7].

The wavelength of light reaching the detector is measured after a light beam passes through an object. The wavelength is used to determine the chemical structure and quantity of molecules present. As a result, both quantitative and qualitative data can be collected. In the wavelength range of 160 to 3500 nm, information can be collected as transmittance, absorbance, or reflectance of radiation. Electrons are promoted to excited states or anti-bonding orbitals as a result of incident energy absorption. Photon energy must match the energy required by the electron to go to the next higher energy state for this transfer to take place. The essential operating principle of absorption spectroscopy is this mechanism. There could be three different sorts of ground state orbitals involved:

i. Bonding molecular orbital:.σ,π
ii. Non-bonding atomic orbital: n
iii. Anti-bonding molecular orbital: σ* ,π*

Transition which involves excitation ofelectron from s bonding orbital to σ anti-bonding orbital is called σ to σ* transition. Likewise, π to π* represents the excitation of an electron of a lone pair (non-bonding electron pair) to an antibonding π orbital. Electronic transitions occurring due to absorption of UV and visible light are:

i. σ to σ*;
ii. n to σ*;
iii. n to π*;
iv. π to π*[3].

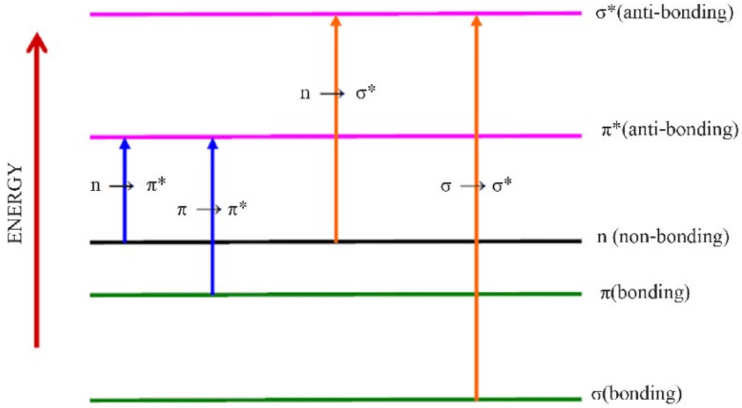

Figure - 2.9: Electron transitions in UV-Vis spectroscopy

When a given wavelength and energy of light is focused onto a sample, it absorbs some of the incident wave's energy. A photo detector detects the sample's absorbance and measures the energy of transmitted light from the sample. The wavelength is used to generate the absorption or transmission spectrum of the light absorbed or transmitted by the sample. The Lambert-Beer rule (Figure 2.7), is a fundamental principle of quantitative analysis that states that a solution's absorbance scales directly with its analyte concentration. The absorbance (unit less) A is defined as the molar absorptivity of the absorbing species (M-1 cm-1), b is the sample holder path length (usually 1 cm), and c is the solution concentration (M) [8].

UV−Vis−NIR spectrometer can monitor absorbance or transmittance in UV – visible wavelength range. The relation between incident light of intensity 'Io' and transmitted light of intensity 'I' is described as follows [8].

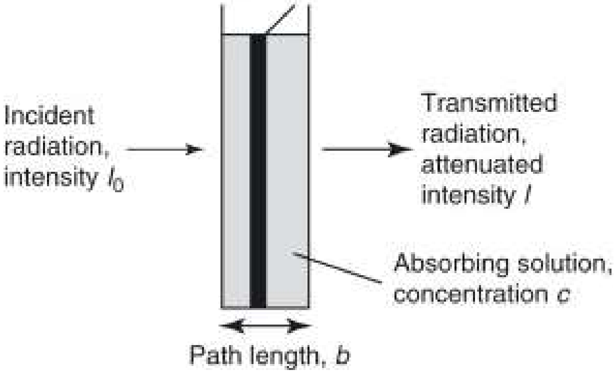

Figure - 2.10: Lambert−Beer Rule

Transmittance, T=$\frac{I}{I_0}$; Transmission rate, T% = $\frac{I}{I_0} \times 100$

Absorbance, A is defined as logarithmic inverse of transmittance, i.e. A = log $(\frac{1}{T})$

$$\log(\frac{1}{T}) = \log(\frac{I_0}{I}) \quad .... (1)$$

We know $I = I_0 e^{-kcl}$ or, T= $\frac{I}{I_0} = e^{-kcl}$ ..... (2)

$$A = \log(\frac{1}{T}) = kcl \quad .....(3)$$

The constant of proportionality, 'k', is used here. While transmittance is unaffected by sample concentration, absorbance is proportional to both sample concentration (Beer's law) and optical path (Bouguer's law). Furthermore, when the optical path is 1 cm and the concentration of the targeted substance is 1mol/l, k is denoted as $'\varepsilon'$ and is characterised as molar absorption coefficient. The material's molar absorption coefficient is representative of the material under specified conditions. The Lambert Beer rule is based on the assumption that there is no stray, produced, scattered, or reflected light.

Components

The spectrophotometer is the instrument used in ultraviolet-visible spectroscopy. It compares the intensity of light before it goes through a sample and measures the intensity of light before it passes through the sample.

The essential components of a spectrometer are -

i. **UV Light Source**

   Electrically igniting deuterium or hydrogen at low pressures produces a continuous UV spectrum. Both deuterium and hydrogen lamps emit light with wavelengths ranging from 160 to 375 nm [3].

ii. **Visible Light Source**

   The radiation source is usually a Tungsten filament (300–2500 nm), a deuterium arc lamp (190–400 nm), a Xenon arc lamp (160–2,000 nm), or, more recently, light emitting diodes (LED) for visible wavelengths.

iii. **Monochromator & Cuvettes**

   A monochromator source is employed, and light is separated into two halves of identical intensity via a half-mirror splitter before reaching the sample. One component (or sample beam) passes through a cuvette containing a clear solvent solution of the material to be studied. The second beam, sometimes known as the reference beam, travels through a comparable cuvette that contains only solvent. Containers for the reference and sample solutions must be transparent to the passing beam.

iv. **Detector**

   The intensity of light transmitted by cuvettes is detected by the detector, which delivers the data to a metre, which records and displays the values. The intensities of light beams are calculated and compared by electronic detectors. Several UVVis spectrophotometers contain two detectors – a phototube and a photomultiplier tube – and simultaneously monitor the reference and sample beams. CCDs (Charge-Coupled Devices) are similar to diode array detectors.

v. **Recording devices**

Most of the time, the amplifier is connected to a computer via a pen recorder. The computer saves all of the information and generates the spectrum of the desired molecule. The following functions can be recalled or continuously monitored by a microcomputer with completely automated equipment, depending on the sophistication of the software:

i. Base-line correction
ii. Conversion of analog to digital (a/d) data
iii. Conversion of extinction values to concentrations [8].

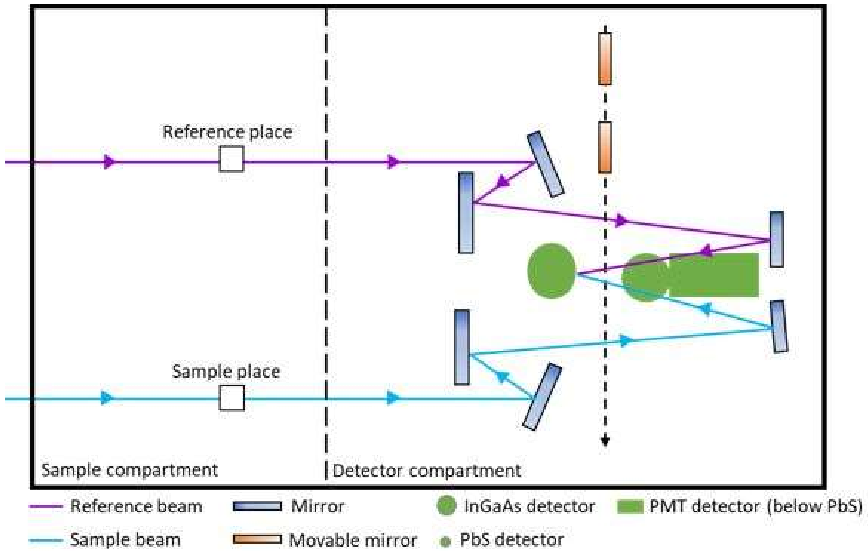

Figure - 2.11: UV−Vis−NIR Spectrometer [8]

Applications:

a) **Qualitative& Quantitative analysis:** UV-Vis absorption spectroscopy can be used to identify substances that absorb UV light. The absorption spectrum is compared to the spectra of recognised chemicals for identification. Aromatic compounds and aromatic olefins are commonly studied using UV-Vis absorption spectroscopy [9].

UV-Vis Spectroscopic measurements can also be used to determine the quantity of a sample.

b) **Structure elucidation of organic compounds:** UV-Vis spectroscopy is important in elucidating the structure of organic molecules, determining the presence or absence of unsaturation, and determining the presence of hetero atoms. The location and combination of peaks can be used to determine if the chemical is saturated or unsaturated, whether hetero atoms are present or not, and so on.

c) **Impurities Detection:** One of the most effective ways for determining contaminants in organic molecules is UV-Vis absorption spectroscopy. Due to contaminants in the sample, additional peaks can be seen, which can be compared to those of normal raw material. Impurities can be determined by measuring absorbance at a given wavelength as well [9].

d) **Instrument Specifications**

a) Name: JASCO UV-VIS Absorption Spectrophotometer

b) Model: V-630

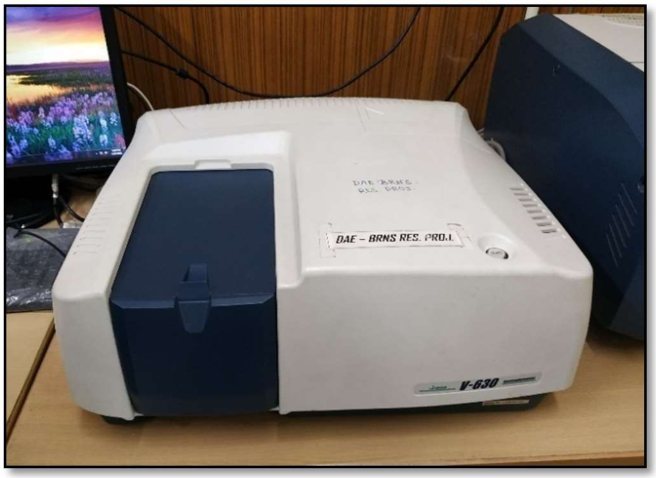

Figure - 2.12: JASCO UV-VIS Absorption Spectrophotometer

2.2.3. Fluorescence Spectroscopy

Lasers have long played a vital part in spectroscopy, which has made a significant contribution to the current state of atomic and molecular chemistry. In chemistry and physics, fluorescence spectroscopy and time-resolved fluorescence are generally used as research methods. Fluorescence is the virtually instantaneous absorption of light energy by molecules at one wavelength and subsequent reemission at another, usually longer wavelength. Fluorescent chemicals have two distinct spectra: an excitation spectrum (the wavelength and amount of light absorbed) and an emission spectrum (the wavelength and amount of light emitted). Fluorometry is a highly specific analytical technique because of this premise. Fluorescence is measured using fluorometry. A fluorometer, sometimes known as a fluorimeter, is a device that measures fluorescence. A fluorometer produces the wavelength of light needed to ignite the analyte of interest, selectively transmits the wavelength emitted, and then measures the intensity of the emitted light. When compared to other analytical techniques, fluorometry is chosen for its exceptional sensitivity, high specificity, simplicity, and low cost. Fluorometry is more sensitive than absorbance measurements in most cases. It is an important analytical tool for both quantitative and qualitative research. [10]

Photon emission mechanisms such as fluorescence and phosphorescence occur during molecular relaxation from electronic excited states. Transitions between electronic and vibrational states of polyatomic fluorescent molecules are involved in these photonic processes (fluorophores). Fluorophores are the most important component of fluorescence spectroscopy. The components of molecules that cause them to glow are known as fluorophores. Fluorophores are mostly molecules with aromatic rings, such as Tyrosine, Tryptophan, Fluorescein, and so on.

Fluorescence: Prompt fluorescence: $S1 \rightarrow S0 + h\nu$

The release of electromagnetic energy is immediate or from the singlet state.

Delayed fluorescence: $S1 \rightarrow T1 \rightarrow S1 \rightarrow S0 + h\nu$

This result comes from two intersystem crossings, at first from singlet to triplet, and then again from triplet to singlet.

Phosphorescence: $T1 \rightarrow S0 + h\nu$

Delayed release of electromagnetic energy from the triplet state [10].

Spectrofluorometer

A spectrofluorometer is a device that uses the fluorescence properties of certain substances to provide information about their concentration and chemical environment in a sample. The emission is monitored at a single wavelength or a scan is done to record the intensity versus wavelength, commonly known as an emission spectrum, when a specific excitation wavelength is chosen.

High-intensity light sources are typically used in spectrofluorometers to blast a sample with as many photons as feasible. This allows the greatest number of molecules to be in an excited state at any given time. Normally, the fluorescence is collected at a 90-degree angle to the optical axis set by the excitation light beam in all of the devices. Instead of measuring the difference in intensity of two signals, which is measured in a spectrometer, a spectrofluorometer measures a signal over a zero background. The light source, monochromator, and light detector are the three main components of a spectrofluorometer.

Light Source: A spectrofluorometer uses a high-pressure xenon arc lamp as its light source. This lamp's bulb contains high-pressure xenon, which is stimulated to a higher level by an electrical arc created by current flowing through the electrodes. The spectrum of light emitted ranges from roughly 250 nm to 1100 nm.

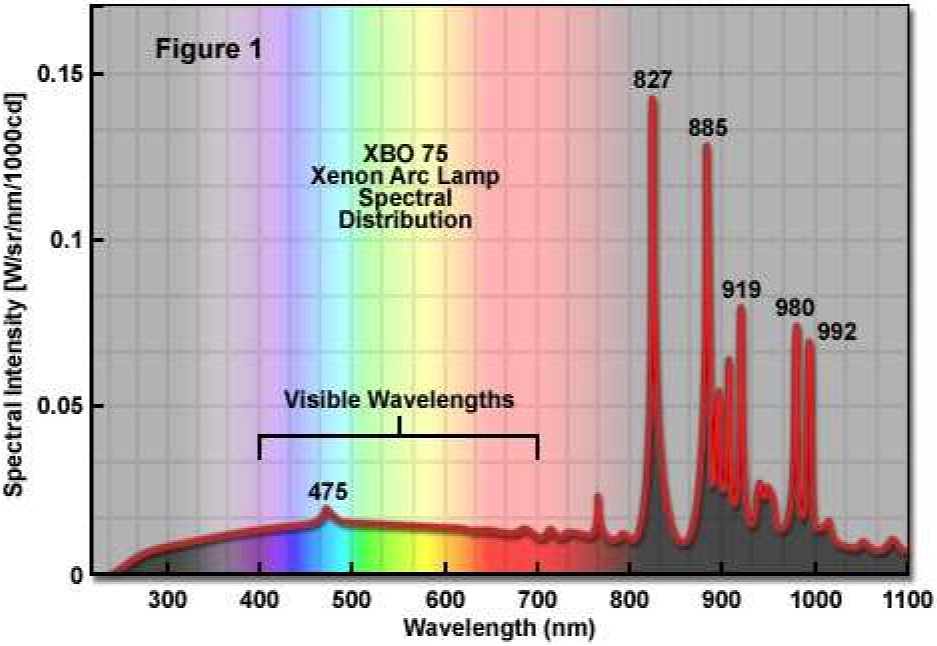

Fig. 2.13: Spectral distribution for the 300W xenon arc lamp [11]

When utilising a xenon arc lamp, monochromators are used to pick the wavelength for irradiating the sample; in the collection channel of a spectrofluorometer, they are used to record the range of wavelengths produced by a fluorophore. A diffraction grating with slits at the entrance and output make up the simplest monochromator. When light strikes the grating at an angle, it diffracts into a succession of angles, the first of which is usually chosen for measurement. When a monochromator is adjusted to deliver radiation at wavelength λ, it also delivers radiation at wavelength 2λ.The second order's strength is typically roughly a tenth of the first order's; yet, this is enough to pollute the emission spectrum. With a judicial selection of filters, the second order can be removed. The amount of stray light, or radiation present at any wavelength other than the targeted wavelength, is a characteristic of every monochromator. For reducing stray light, various solutions are possible, the first of which is a judicious grating selection. The ruled grating and the holographic grating are the two types of grating. To construct a monochromator, gratings can be arranged in a variety of ways, the two most prominent being the Czerny-Turner and the Seya-Namioka.

A photomultiplier tube (PMT) or photodiode is a light detector that converts light into an electrical signal. The PMT can be used in the wavelength range of 230 nm to 830 nm. It is clear that the sensitivity is not the same even within the working wavelength range, and the results must be corrected.

Polarizers are used in spectrofluorometers to measure anisotropy. The superposition of the wavelength transmission of the various parts of the instrument defines the operational zone of the instrument. Even when measuring fluorescence parameters inside this zone, the variance in transmission must be taken into account. Photomultiplier tubes are used to detect the fluorescence, which is then quantified using the proper electronic instruments. Typically, the output is presented in a graphical format and saved digitally [11].

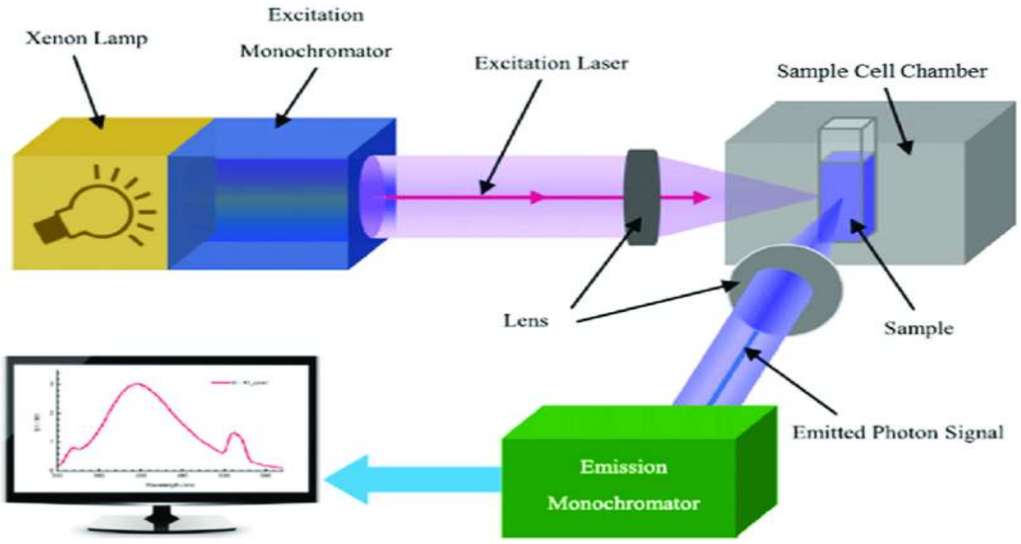

Figure - 2.14: Schematic Diagram of Arrangements in a Spectrofluorometer [12]

- **Applications of Fluorescence Spectroscopy**

a) **LIF Spectroscopy in cancer diagnosis:** Laser spectroscopic techniques have the potential for in-situ, near real-time diagnosis, and the use of non-ionizing radiation assures that the diagnosis can be repeated without harm. In two techniques, laser induced fluorescence (LIF) has been used to diagnose cancer. One strategy is to give a medication like hematoporphyrin derivative (HpD) to the patient, which is selectively retained by the tumour. When the medicine is photo stimulated with the right wavelength of light, it fluoresces in the tumour. The tumour is detected and imaged using this fluorescence. Intersystem crossover also leads to the populating of the triplet state as a result of photo excitation. The molecule in the excited triplet state can either react directly with biomolecules or produce singlet oxygen, which is harmful to the host tissue. Photodynamic treatment of tumours takes advantage of the resultant damage of the host tissue [10].

b) **Glucose Determination:** Blood glucose levels (fasting, pp) are very good predictor of human health. An abnormally high level of glucose can reveal a lot about disorders like diabetes or hypoglycemia. Fluor photometry is frequently utilised because to its ease of use and great sensitivity.

c) **Bioscience:** Fluorescence spectroscopy can be used to sequence DNA. A DNA sample is put into a fluorescence spectrometer with an extrinsic fluorophore to acquire a reading of the sample's concentration.

d) **Agriculture:** Spectroscopic techniques are frequently used to identify various crop kinds. Citrus seedling varieties can be identified using the laser-induced fluorescence emission approach.

- **Study of Marine Petroleum Pollutants:** Fluorescence spectroscopy is a useful technique for detecting oil slicks on the water's surface, determining petroleum pollutants in saltwater, determining specific petroleum derivative compounds, and identifying pollution sources [10].

Instrument Specifications

Instrument Name: JASCO Spectrofluorometer

Instrument Model: 8200

Figure - 2.15: JASCO Spectrofluorometer

2.2.4. Nuclear Magnetic Resonance (NMR) Spectroscopy

Introduction

The spectroscopic technique of nuclear magnetic resonance spectroscopy is used to study local magnetic fields surrounding atomic nuclei. Certain nuclei resonate at a specific frequency in the radio frequency band of the electromagnetic spectrum when exposed to a strong magnetic field. Slight fluctuations in this resonance frequency provide extensive information about the atom's molecular structure. According to the NMR principle, many nuclei have spin and all nuclei are electrically charged. When an external magnetic field is applied, energy can be transferred from the base energy to a higher energy level [13].

i. Nucleus are electrically charged and many of them have spin.
ii. Upon applying external magnetic field, energy transfer is possible from minimum base energy to higher energy levels.
iii. Energy transfer takes place at a frequency that resonates with radio frequency.
iv. Energy is emitted at the same wavelength when the spin comes back to its base level.
v. As a result, the processing of the NMR spectrum for the concerned nucleus is yielded by measuring the signal that matches this transfer [13].

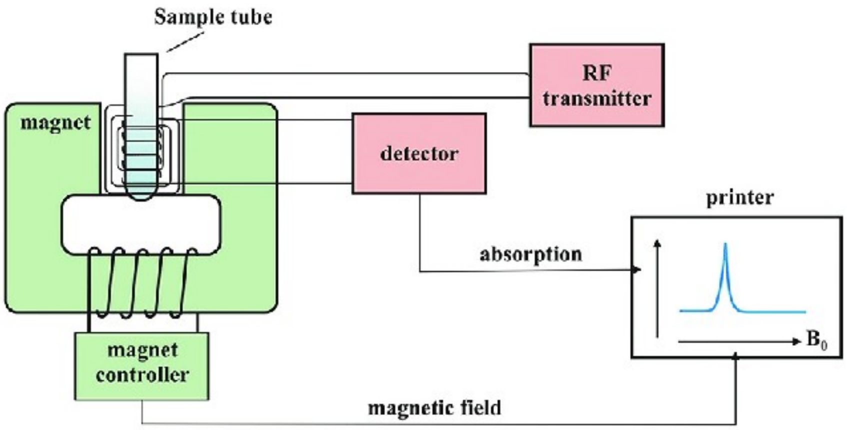

Figure - 2.16: Diagram of a NMR Spectrometer [13]

NMR Spectroscopy Hardware

Hardware in NMR spectroscopy consists of nine major parts. In the following, they have been briefly discussed:

1. **Sample tube –** It is a glass tube which is 8.5 cm long and 0.3 cm in diameter.
2. **Magnetic coils–**Magnetic coil generates magnetic field whenever current flows through it
3. **Permanent magnet –** It helps in providing a homogenous magnetic field at 60 – 100 MHZ
4. **Sweep generator –** Modifies the strength of the magnetic field which is already applied.
5. **Radiofrequency Transmitter –** It produces a powerful but short pulse of the radio waves.
6. **Radiofrequency Receiver–** It helps in detecting receiver radio frequencies.
7. **RF Detector –** It helps in determining unabsorbed radio frequencies**.**
8. **Recorder –** It records the NMR signals which are received by the RF detector.
9. **Display system –** A computer that display the records the data [13].

- **Applications**

i. NMR spectroscopy is a spectroscopic technique used by chemists and biochemists to study the characteristics of organic molecules, while it can be applied to any sample with spin-containing nuclei.
ii. NMR can be used to analyse mixtures containing known substances quantitatively. NMR can be used to compare unknown chemicals to spectral libraries or to derive their basic structure directly.
iii. NMR can be used to assess molecule conformation in solutions as well as to examine physical features at the molecular level such as conformational exchange, phase shifts, solubility, and diffusion after the basic structure is known.[13]

2.2.5. Time Resolved Spectroscopy

Time Resolved Spectroscopy is a type of spectroscopy that is used to track interactions between molecules and short-term motions. It is a helpful approach in bimolecular structure characterization and dynamics because it can quantify changes in the picosecond or nanosecond time range.

TCSPC: Time correlated single photon counting

TCSPC [15] is based on the detection of single photons in a periodic light signal, measurement of the individual photon detection times, and reconstruction of the waveform from the individual time measurements. The method takes advantage of the fact that the light intensity for low-level, high-repetition-rate signals is typically so low that the likelihood of detecting one photon in a single signal period is substantially lower than one. As a result, the detection of multiple photons can be ignored, and the method depicted in Figure 2.13 can be employed instead:

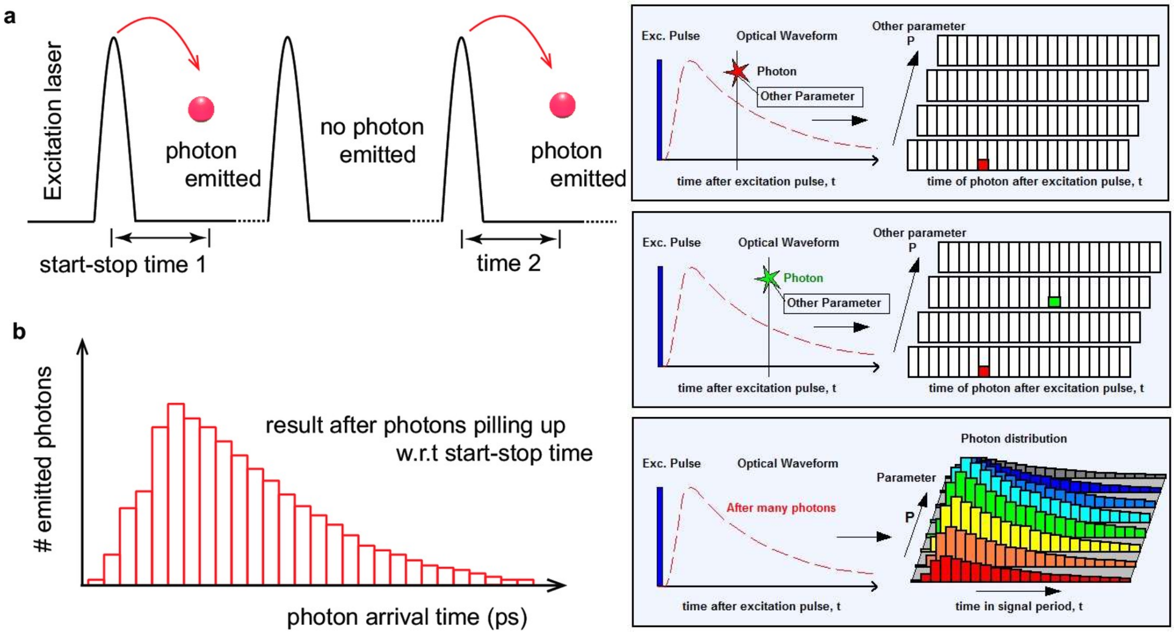

Figure - 2.17: a) TCSPC Measurement Technique [16] **(b)** Multi-Dimensional TCSPC [15]

Due to the detection of individual photons, the detector signal consists of a train of randomly distributed pulses. Many signal intervals are devoid of photons, whereas others contain a single photon pulse. Periods with multiple photons are extremely rare. The time of the matching detector pulse is measured when a photon is detected. The events are stored in memory by inserting a '1' in a memory location according to the detection time. The histogram of detection timings, i.e. the waveform of the optical pulse, grows up in the memory after many photons. Despite the fact that this approach appears to be hard at first glance, it has a number of significant advantages:

i. TCSPC's temporal resolution is limited by the transit time spread, not the width of the detector's output pulse.
ii. Because TCSPC has a near-perfect counting efficiency, it achieves the best signal-to-noise ratio for a given number of photons detected.
iii. TCSPC is able to record the signals from several detectors simultaneously
iv. TCSPC can be employed in confocal and two-photon laser scanning microscopes as a high-resolution high-efficiency lifetime imaging (FLIM) technology when paired with a fast-scanning technique.

v. TCSPC can collect fluorescence lifespan and fluorescence correlation data at the same time.

vi. TCSPC devices with cutting-edge technology achieve count rates in the MHz range and acquisition times of a few milliseconds [15].

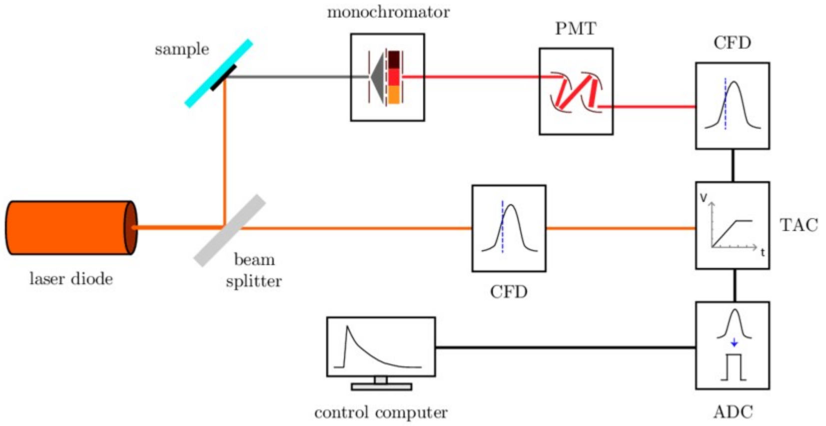

Figure - 2.18: Block diagram of TCSPC using Laser Diode.

Here, CFD = Constant Fraction Discriminator, TAC = Time to Amplitude Converter, ADC = Analog to Digital Converter [17]

Applications:

- Fluorescence microscopy,
- TCSPC also has many applications in diverse areas of Science & Technology.
- Wide-field photon counting detectors are used in optical communications systems, and recent breakthroughs in superconducting detector and SPAD array technology can be credited to the rapidly expanding applications in these fields [18].

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CHAPTER: 3

Photophysical studies of a novel synthesized Dyad and its nanocomposite forms in Chloroplast environment

3.1. Abstract

Steady state and time resolved spectroscopic studies were made to examine how photophysical properties of a pristine short-chain dyad (E)-(((9H-fluorene-2-yl)imino)methyl)-N,Ndimethylaniline (NNDMBF) and its nanocomposite forms when combined with Carbon quantum dots (CQDs), Graphene oxide (GO) as well as reduced Graphene oxide (RGO) alter significantly in the presence of Chloroplast (**clp**). These studies were made to examine whether within the **clp** the highly efficient nanocomposite systems could retain their properties to serve as artificial light energy converters and charge storage systems. The present experimental findings hint that the stability of trans conformation of the nanocomposite dyad,specially in CQD which is primarily due to surface trap effects reduces significantly in **clp** environment. In the trans conformation, the positioning of the atoms may force them closer together, increasing the amount of steric strain in the molecule. But in presence of **clp** , retention capability of trans-conformer in the excited state of the dyad becomes weakened in the case of its nanocomposite forms with CQD, GO (or RGO) with concomitant predominance of the folded cis-form. Thus the present time resolved studies demonstrate that **clp** environment favors considerably the energy wasting charge-recombination reactions rather to the formations of charge-separated species. The present results demonstrate that **clp** is not a favorable medium for the construction of artificial light energy converters, though within this environment efficiently photosynthesis occurs through energy transfer followed by photoinduced electron transfer reactions. However, the present investigation demonstrates that **clp** environment enhances the photoswitchable character of the nanocomposite systems. A plausible interpretation of this environmental behavior in **clp** may be due to the strong interaction between the amino-group present in the donor part of the dyad and oxygen groups of the chlorophyll.

Key words: Graphene oxide, Reduced graphene oxide, Trans-conformer, Photoswitchable dyad, Nanocomposites, Chloroplast, Light energy converter, Time resolved spectroscopy, Charge-separated species, charge recombination

3.2. Introduction

Spectroscopic studies on photoswitchable short-chain dyads [1–8] are gradually becoming topics of modern research due to their wide applications in molecular electronics, building of artificial light energy conversion devices, optical data storage systems etc. Also, the technological advantages of nanoparticles for its various applications as nanocomposites are its high stability and carrier capacity [9–15]. Lately studies by steady state and time resolved spectroscopic techniques demonstrate that when the short-chain dyad NNDMBF combines with CQD [1], GO and RGO [2] nanoparticles they exhibit better artificial light energy conversion materials relative to pristine dyad (p-dyad).

From time resolved spectroscopic measurements it was observed that retention capability of ground state trans conformer of the dyad increases profoundly, especially in the case of carbon quantum dots (CQD), even in the excited state on photoexcitation [1]. Trans-form being of elongated nature charge-separated species formation is highly favored over folded cis –form which is responsible for charge recombination process. In case of p-dyad, ground state trans-conformer of the dyad converts fully into the cis form in the excited state on photoexcitation. Thus nanoparticles in the nanocomposites of the dyad possess great role to increase the charge-separated rate. From these observations it indicates that these nanocomposites may serve as efficient artificial light energy converters. In the present investigations a novel synthesized dyad NNDMBF has been chosen where N, N-dimethyl amino donor is being attached with the acceptor fluorene (F) **(Figure 1**). By using steady state and fluorescence lifetime techniques it was observed that in the environment of **clp** these nanocomposites somewhat suffer lacking in the retention capability of trans-form (elongated structure) in the excited state increasing the possibility of occurrences of energy wasting charge recombination process due to predominance of folded (cis) form. Detailed time resolved spectroscopic measurements were made to compare the efficiency of light energy conversion of the pristine dyad and when it adsorbs the nanosurfaces of CQD, GO and RGO ie., of the same dyad in nanocomposite forms and finally when the nanocomposites are incorporated in **clp** environment. The results are described below.

3.3. Experimental details

3.3.1. Materials

The method of synthesis and characterization of the short chain dyad (E)-4-(((9H-fluorene-2-yl)imino)methyl)-N,Ndimethylaniline(NNDMBF) are described elsewhere [3]. The solvents acetonitrile (ACN) (SRL), and cyclohexane (CH) (Sigma Aldrich) of spectroscopic grade were purified following the standard procedures and tested before use for the absence of any impurity emission in the concerned wavelength region. Water was deionized using a Millipore Milli-Q system. The solutions were prepared by dissolving the appropriate amount of dyad in ACN, CH and **clp**. The synthesis and structural characterizations of GO and RGO are described in our earlier paper [2]**.**

3.3.2. Isolation of Chloroplast

Young and fully expanded deveined mung bean leaves were ground with a blender in a medium containing mannitol, HEPES, EDTA, $MgCl_2$ and BSA in ice cold conditions. In brief, the leaves were homogenized in a chloroplast isolation buffercontaining 330 mM mannitol, 30 mM HEPES, 2 mM EDTA, 3 mM $MgCl_2$ and 0.1 % w/v BSA (pH 7.8) using a blender for 15s. The slurry was filtered through 8-layers of cheese cloth followed by centrifugation at 250 g for 5 min. The supernatant was again centrifuged at 1000g for another 5min. The chloroplast was washed and resuspended in an extraction buffer and used for tracking the photosynthetic pathway.

3.3.3. Spectroscopic Apparatus

UV–vis absorption and steady state fluorescence emission spectra of dilute solutions of the dyad were recorded at the ambient temperature (296 K) using 1 cm path length rectangular quartz cells by means of an UV–vis absorption spectrophotometer (JASCO UV–Vis absorption spectrometer, Model: V-630) and JASCO spectrofluorimeter (Model: 8200) respectively.

Fluorescence lifetimes were determined by using a time correlated single-photon-counting (TCSPC) technique with the model FLUOROLOG TCSPC HORIBA JOBIN YVON using nanosecond diode lasers of 375 nm and 440 nm (Horiba scientific, DD-375L) as excitation source profiles. The decay kinetics are monitored at emission wavelengths of 480 nm and 550 nm. The quality of fit is assessed over the entire decay, including the rising edge, and tested with a plot of weighted residuals and other statistical parameters e.g., the reduced χ2 and the Durbin–Watson (DW) parameters. All the solutions prepared for room temperature measurements were deoxygenated by purging with an argon gas stream for about 30 min.

3.4. Results and Discussion

3.4.1 UV-vis absorption and steady state fluorescence spectra

From the theoretical predictions [1] it is seen that the dyad NNDMBF though in its ground state possesses both cis- and trans-forms but relatively trans-form (elongated nature) appears to be more stable (**Fig. 1**). From the NMR analysis it is apparent that there is a possibility of the co-existence of two conformers: Trans- and Cis- (**Fig. 1**) of the dyad in its ground state. Moreover trans-form of the dyad NNDMBF appears to be more planar.

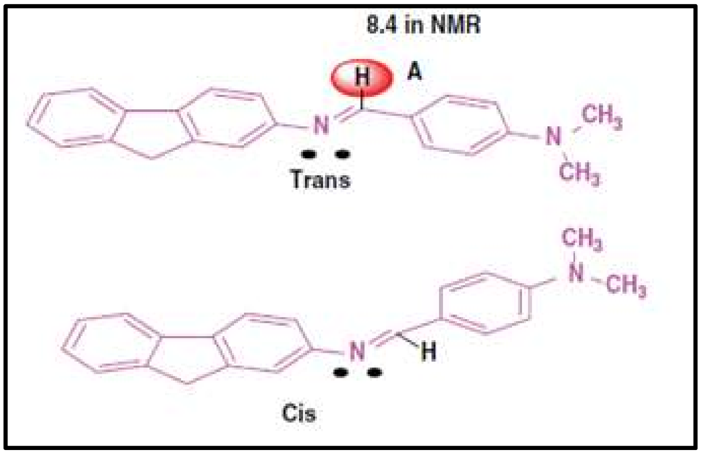

Figure – 1: Cis- and Trans-structure of the dyad NNDMBF

This prediction reflects in the UV–vis spectra of the pristine dyad NNDMBF where a strong charge transfer (CT) band corresponding to the stable trans-isomer was observed at 375 nm and a very weak tail, which may be due to another conformation "cis" of the dyad, is extended down to 450–500 nm region (**Fig. 2**).

UV-vis absorption spectra of the pristine dyad in ACN solvent exhibits a broad long wavelength band at around 365 nm region **(curve 1 of Fig 2)**. The charge transfer nature of this broad band has been confirmed from solvent polarity effect which exhibits blue shift in nonpolar environment relative to ACN solvent. This CT band originates due to partial transfer of electron from the highest occupied molecular orbital (HOMO) of the donor chromophore (D) to the lowest unoccupied molecular orbital (LUMO) of the acceptor fluorene (A). It is to be pointed out here that the UV-vis absorption spectra of the mixture of the free donor and acceptor components (when not present in the dyad) in ACN medium correspond to the superposition of the corresponding spectra of the donor and the acceptor moieties (**Fig 3**).

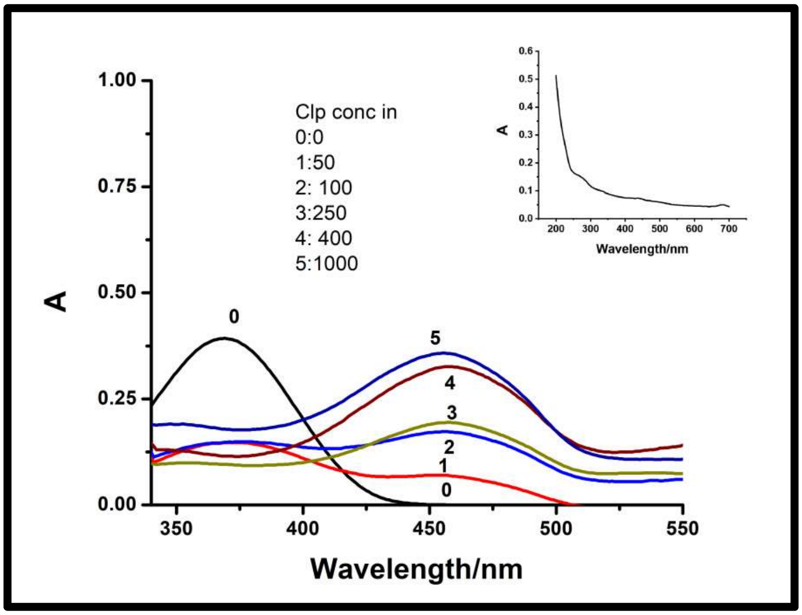

Figure – 2: UV-vis absorption spectra of the pristine dyad (P-dyad) (Curve 0) and in presence of different concentrations (μg/ml) of **clp** at the ambient temperature (curves 1 to 5) inset: the UV-vis spectra of **clp at** the conc 1000 μg/ml.

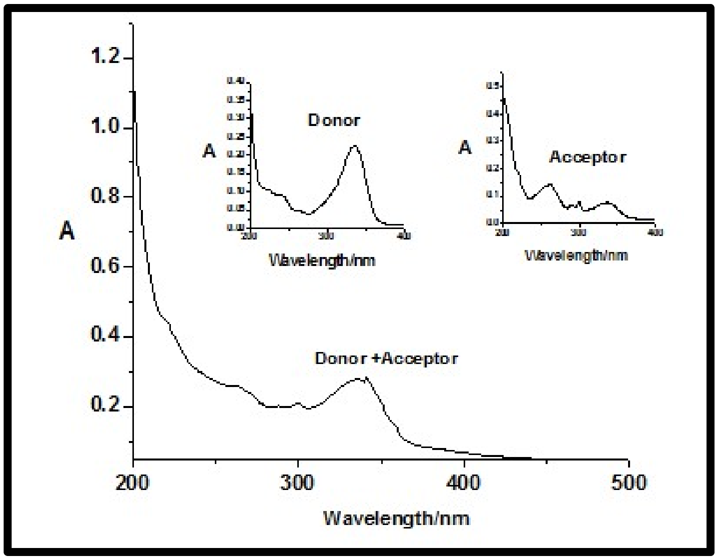

Figure – 3: UV-vis absorption spectra of the mixture of the donor and the acceptor in ACN medium. Inset: (right) UV-vis spectra of the acceptor and (left) UV-vis spectra of the donor only

This indicates the lack of formations of intermolecular ground state complex between the donor NNDMB and acceptor (F). However, in case of the dyad, intramolecular interaction between the donor NNDMB and the acceptor Fluorene (F) leads to the formation of Charge transfer band (broad band at 365 nm region). This indicates that within the dyad, the alignment of the donor and the acceptor moieties are such that it facilitates the formation of CT spectra in the ground state.

With addition of **clp** (**Fig 2**) 365 nm band diminishes gradually with the concomitant augmentation of another band near 450 nm region. Following the observations made earlier with gold nanoparticles of different morphologies [3-5] and also it appears that when the dyad adsorbs on the surface of GO or RGO [2], the band associated with the cis- conformation develops, peaking at about 440 nm, through interconversion (trans to cis) process in the ground state. The similar finding is observed in the case of **clp** also. In inset of figure 2 the UV-vis spectra of **clp at** the conc 1000 µg/ml show negligible absorbance. Thus the band at the region of 450 is not due to **clp** itself.

On exciting the CT absorption band of the dyad NNDMBF-clp system (CT nature has been conformed from the solvent polarity effect) at 365 nm region, CT fluorescence band envelop at around 400 nm to 550 nm was observed (**Figs 4)** along with a very weak shoulder –like band at

500 nm region. The 450 nm band is found to be diminished significantly unlike the nature of the band located at 500 nm which remains practically unaffected with increase of concentrations of

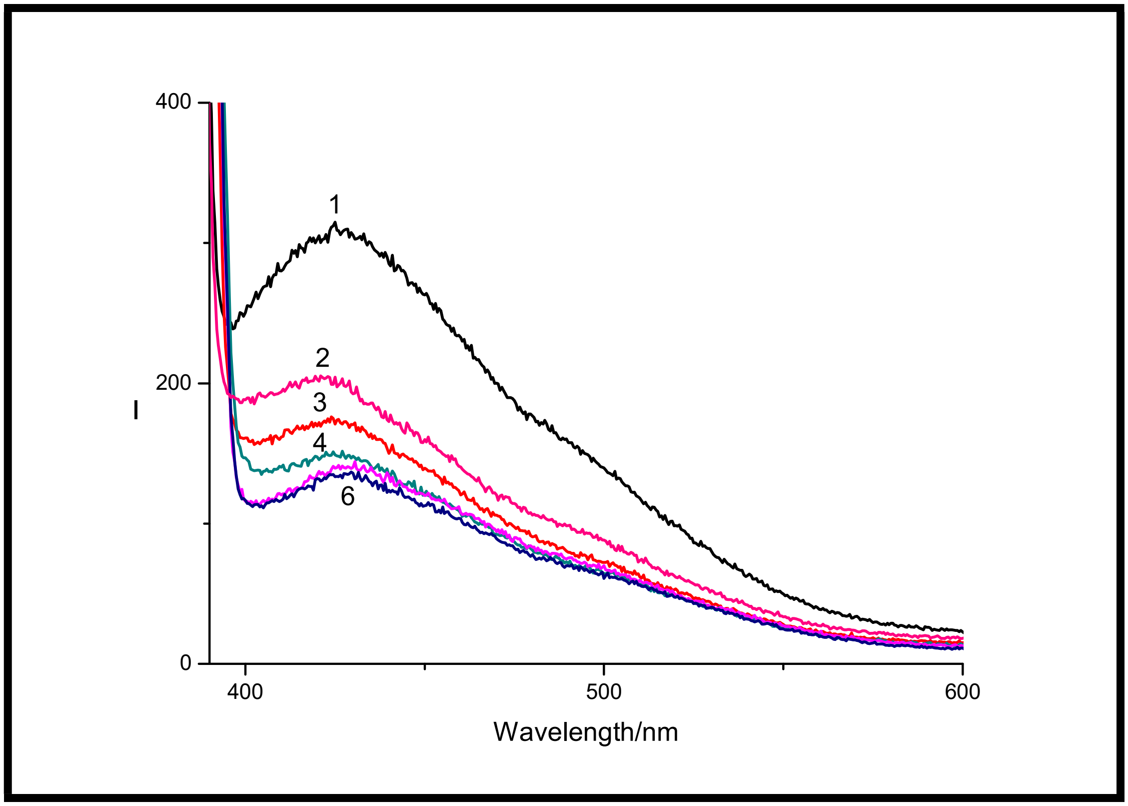

Figure – 4: Fluorescence CT emission spectra (exc~ 365 nm) of dyad NNDMBF in presence of **clp** of conc. (µg/ml) in 1: 0; 2: 100; 3: 200; 4: 300; 5: 400; 6:700

clp (Fig 4). The above findings demonstrate that even with the 365 nm excitation (region of mostly trans-isomers) emitting region of cis-isomer at 550 nm appear to be formed in the excited state. This observation demonstrates that photoswitchable conversion of the trans-dyad to the cis-form facilitates both in p-dyad and when combined with **clp.** This is contrary to the situation when the dyad combines with several nanoparticles eg. Graphene oxide (GO), reduced grapheme oxide, carbon quantum dots (CQD) etc where only enhancement of the entire band envelop was observed [**1, 2**]. In these cases, from the observed enhancement of the fluorescence band throughout its entire region indicates that both trans- and cis –species are formed by exciting the ground state trans-conformers. With addition of **clp**, it appears that on photoexcitation, formations of only cis forms of the dyad prevail at the expense of the photoswitchable conversion of ground trans form. Similar observations were also found when the nanocomposite dyads (p-dyad+ CQD, p-dyad+GO, p-dyad+RGO) combines with **clp**. Thus in presence of the chloroplast it shows that this environment impedes the capabilities for retaining trans conformer in the excited state. In absence of **clp**, formations of large amount of trans isomers relative to cis-ones, due to reduction of photoswitchable nature, was found in the excited state, especially in the case of dyad-CQD systems [1]. Thus it shows **clp** acts as an inhibitor for the charge-separated species formation. Fluorescence lifetime measurements were made to corroborate this presumption.

3.4.2 Fluorescence lifetime measurements by TCSPC method

The fluorescence lifetimes of the dyad were determined by using the time correlated single photon counting (TCSPC) technique (**Fig. 5**). By monitoring the different positions (480 nm (trans-region) and 550 nm (primarily cis-domains)) of the steady state fluorescence spectra the possibility of formations of different conformers in the excited state due to photo excitation has been examined. These findings (**Table 1**) further substantiate our ideas that the present short-chain dyad NNDMBF possesses primarily photoswitchable character, both in its pristine form and in **clp** environment. It was also found that the nanocomposite dyads which exhibit large fraction of trans-conformers on photoexcitation [1-3] suffer diminution in presence of **clp** facilitating cis-form to prevail.

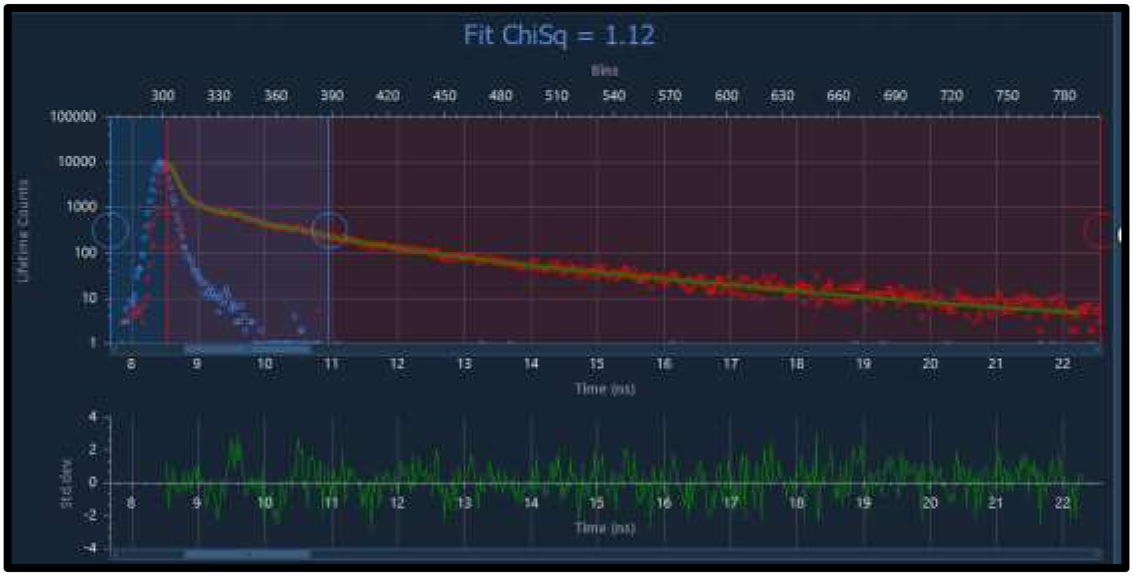

Figure – 5: Fluorescence decay of the dyad –clp system in ACN-sucrose solution, ex =375 nm, em = 480 nm, the fast (blue) decaying component represents impulse response (diode laser) (χ^2~ 1.12). The residual is also shown.

In case of the pristine dyad NNDMBF when excitation was made at 375 nm (by using diode laser), it was found that at the monitoring wavelength 480 nm (the peak region), majority emission originates from a species having lifetime of 15 ps. (**Table 1**). On monitoring at the 550 nm region again only faster component of lifetime of picoseconds (ps) order was observed.

Similar findings were observed in presence of **clp** also thus it is apparent that on photoexcitaion the dyad in its prestine form and also in **clp** environment photoswitches from trans to cis form.

On comparing the results of the related fractional contributions (f) (**Table 1**) of dyad+CQD, dyad+GO and dyad +RGO without adding **clp** and in presence of clp**,** it indicates that in the environment of **clp** contribution from cis-conformeris significant. From these results it could be inferred that for the nanocomposites in the environment of **clp** the capability of retention of ground state trans-conformation in the excited state due to photoexcitation reduces considerably. Thus in the excited state due to prevalence of cis-form charge recombination process will dominate relative to charge-separated one. From the fluorescence excitation spectra of dyad-clp system (**Fig 6**) it shows that 550 nm fluorescence band originates from both 450 nm (region of cis-conformer) and 379 band (mostly trans-regime). Thus 550 nm band is generated due to single species cis; directly from ground cis located at 450 nm and by photoconversion of trans, located mostly at 379 nm region.

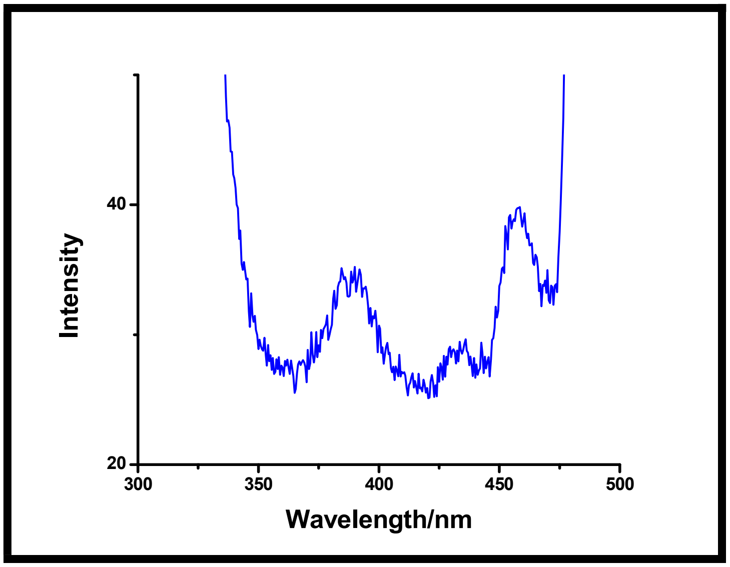

Figure – 6: Fluorescence excitation spectra of the dyad-clp system, mon wavelength ~ 550 nm

Table 1: Fluorescence Lifetime data of the short chain dyad NNDMBF in absence (pristine) (**p-dyad)** and presence of CQD, GO and RGO, clp at the different excitation and emission wavelengths at the ambient temperature. Values in parentheses besides lifetimes correspond to fractional contributions (f) of the particular species in the total steady state fluorescence emission intensity. Comparative studies were made on the fractional contributions of the nanocomposite systems without and in clp environment at the ambient temperature

Samples	**λ_{exc} (nm)**	**λ_{em}(nm)**	**τ_1 (ns)(f_1)**	**τ_2 (f_2)**	**χ^2**
p-dyad	375	480	1.50 (0.06)	15 ps (0.94)	1.09
		550	-	19 ps (1.0)	1.07
			-	-	---
Dyad+clp	375	480	1.00 (0.03)	27ps(0.97)	1.12
		550	1.15 (0.01)	29 ps(0.99)	1.17
Dyad+CQD	375	480	6.40 (0.84)	256ps(0.16)	1.12
		550	6.00 (0.77)	260ps (0.23)	1.15
Dyad+CQD+clp	375	480	6.44(0.20)	219 ps(0.80)	1.18
		550	6.60 (0.15)	268 ps(0.85)	1.16

Contd....... **Samples**	λ_{exc} **(nm)**	λ_{em}**(nm)**	τ_1 **(ns)(f$_1$)**	τ_2 **(f$_2$)**	χ^2
Dyad+GO	375	480 550	3.61(0.27) 3.44 (0.17)	88 ps (0.73) 82 ps (0.83)	1.08 1.09
Dyad+GO+clp	375	480 550	3.90(0.19) 3.20 (0.01)	82 ps (0.81) 80 ps (0.99)	1.08 1.12
Dyad+RGO	375	480 550	3.61 (0.27) 3.00 (0.13)	88 ps (0.73) 87 ps (0.87)	1.14 1.18
Dyad+RGO+clp	375	480 550	3.77 (0.21) 3.50 (0.02)	92 ps (0.79) 90 ps (0.98)	1.12 1.15
Dyad + **GQD(1μg/ml)** **Dyad +GQD+clp**	375	480 520 480	54 ps(0.72) 50 ps (0.67) 55ps(0.23)	25ps(0.28) 25 ps(0.33) 22 ps (0.77)	1.11 1.13 1.12

From the steady state and time resolved spectroscopic measurements it has been demonstrated that nearly 80% (as evidenced from fluorescence lifetime determinations) trans structure of the ground state dyad could be protected in the environment of CQD [1] (**Table 1**) even on photoexcitation. As trans conformers facilitate the formation of longer-lived charge-separated species being, in general, of elongated nature than the folded cis-form, the dyad-CQD appears to be better light energy converter or energy-storage device than the p-dyad. One plausible cause for the retention of trans conformer even on photo excitation in cases of nanocomposites (pristine dyad behaves differently) may be due to surface coverage [16, 17] or surface trap **[18]** effect. In favor of proposition of conformational change due to surface coverage effect, the change in conformation (close packing) was found for polymeric chain systems **[17]** with the increase of the degree of the surface coverage area of the polymer on the nanoparticles. It was suggested that in the small size of a CQD (typically 2–5 nm) **[17]** a large fraction of its constituent atoms being on the surface may form the electronic states. These states may act as traps for electrons or holes, or both, localizing them at the surface. These trap states may be responsible to hinder the photoconversion of trans- to cis-isomer of the dyad as surface traps influence charge dynamics on a subnanosecond timescale. It appears that out of the two mechanisms the surface trapping appears to play dominant role in the formation of extended (trans) conformers in case of CQD **[1]**. However, the exact mechanisms are still not clear and to be explored. But the present experimental findings hint that the stability of conformation (trans form in CQD) may be due to primarily surface trap **[1]** (and references therein) effects. In the trans conformation, the positioning of the atoms may force them closer together, increasing the amount of steric strain in the molecule. But in presence of **clp**, retention capability of trans-conformer in the excited state reduces significantly in the case of the nanocomposite dyad-CQD system with concomitant predominance of the folded cis-form. The similar observations were also made for the dyad-GO and dyad-RGO systems in **clp** environment. Thus **clp** environment favors the energy wasting charge-recombination reactions relative to the charge-separated species formations.

The transient absorption measurements at the different delays between exciting and analyzing pulses seem to be helpful to substantiate the fact of prevailing the cis-form in the excited state in the environment of clp. For the present dyad the situation differs (dominance of trans isomer) when it combines with different nanoparticles only, as discussed above, like CQD, GO and RGO etc. In this case the hindrance of trans-cis conversion or stability of trans-structured species of nanocomposite dyad on photoexcitation appears to be due to surface trap effects which seemingly become less effective in presence of the chloroplast. The present investigation demonstrates that **clp** environment enhances the photoswitchable character of the nanocomposite systems and facilitates the occurrences of the energy wasting charge recombination processes due to the predominance of folded cis-conformer at the expense of the formations of charge-separated species. The changes of such properties of nanocomposites when incorporated within **clp** are shown as graphical representation in **Figure 7.** It is apparent from the figure 7 that though nanocomposites show larger retention capability of ground trans corformation even in the excited state but in the environment of **clp** folded cis structure predominates indicating energy wasting charge recombination process will be facilitated. Even in cases of quantum dots (CQD and GQD), significant trans-retention capability of these nanocomposites reduces considerably in chloroplast environment. A plausible interpretation of this environmental behavior in **clp** may be due to the strong interaction between the amino-group present in the donor part of the dyad and oxygen groups of the chlorophyll. Following the observations by Nazri *et al* [19] it appears that the additions of amino groups present in the dyad to the CQD enhance the activity of chlorophyll through electrostatic interactions. This interaction appears to favor the conversion of mostly planar trans-structure of the photoexcited nanocomposite dyad systems into its folded form. Their observed results from density functional theory calculation also confirm the interaction of the NCQD (amino funtionalized Carbon Quantum Dots) with chlorophyll exists, and the strongest interaction occurs between nitrogen sites of the carbon core and the oxygen group of chlorophyll. Further investigations with similar systems are now underway to corroborate the findings.

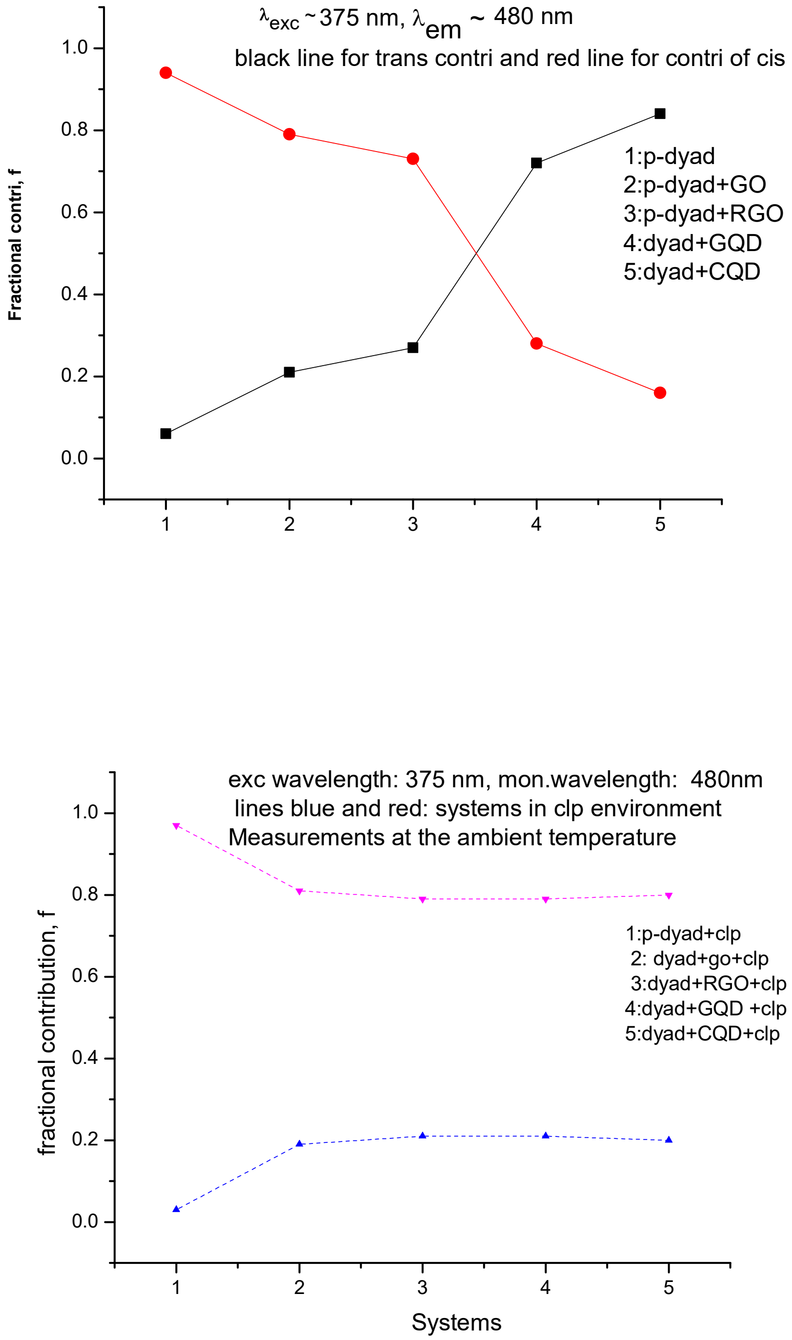

Figure – 7: Changes in trans-and cis- contributions in the cases of pristine dyad (p-dyad) and some of its nanocomposites in absence (upper) and in presence of **clp** environment (lower). In upper curve: black line for trans- and red line for cis- ; In lower curve: blue line for trans- and pink line for cis-**,** (λ_{exc} ~ 375 nm λ_{em}~ 480 nm)

3.5. Conclusions

The present experimental results obtained from time resolved spectroscopic techniques demonstrate that the nanocomposites with CQD, GQD,GO and RGO due to their capabilities for retention of ground state trans-form even in the excited state on photoexcitation, they could be used to building up artificial light energy conversion devices. But these nanocomposite systems suffer reduction considerably in the retention capabilities when incorporated in **clp** environment. Thus it shows **clp** is not a favorable medium for the construction of artificial light energy converters, though within this environment efficiently photosynthesis occurs. Transient absorption spectroscopic measurements are, however, needed for unequivocal assertion of this presumption. Nevertheless the **clp** appears to be an useful environment where photoswitchable character of the nanocomposites becomes more active making their conformations folded in nature. A plausible interpretation of this environmental behavior in **clp** may be due to the strong interaction between the amino-group present in the donor part of the dyad attached to the CQD or other nanoparticles and oxygen groups of the chlorophyll. This interaction of electrostatic in nature appears to be primarily responsible for the conversion of mostly planar trans- structure of the photoexcited nanocomposite dyad systems into its folded form which favors charge recombination. Further investigations with similar systems are now underway to corroborate the findings.

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CHAPTER: 4

Structural behaviour when the novel synthesized Dyad and its nanocomposite forms embedded in Chloroplast environment

The **clp** appears to be an useful environment where photoswitchable character of the nanocomposites becomes more active making their conformations folded in nature.

A plausible interpretation of this environmental behavior in **clp** may be due to the strong non-covalent interaction between the amino-group present in the donor part of the dyad, attached to the CQD or GQD, GO, RGO etc., and oxygen groups of the chlorophyll (mainly of chlorophyll A). This interaction of electrostatic in nature appears to be primarily responsible for the conversion of mostly planar trans- structure of the photoexcited nanocomposite dyad systems into its folded form which favors charge recombination. From the Theoretical predictions by using the open-source program **Autodock vina** , the binding affinity of the amino group of the donor part of the dyad with the oxygen atoms present in chlorophyll A was observed to be -7.52 Kcal M^{-1}**. Figure 4.1** shows the folded structure of the nanocomposite dyad which appears to be dominating in the excited state when immersed in the environment of **clp.** The arrangement of chlorophyll molecules and electron carriers is optimized to facilitate efficient charge separation and transfer. However, the specific spatial organization may also enhance the probability of charge recombination by minimizing the distance between the donor and acceptor and providing favorable folded orientations for the occurrences of faster charge recombination rather than forward photoinduced electron transfer reactions.

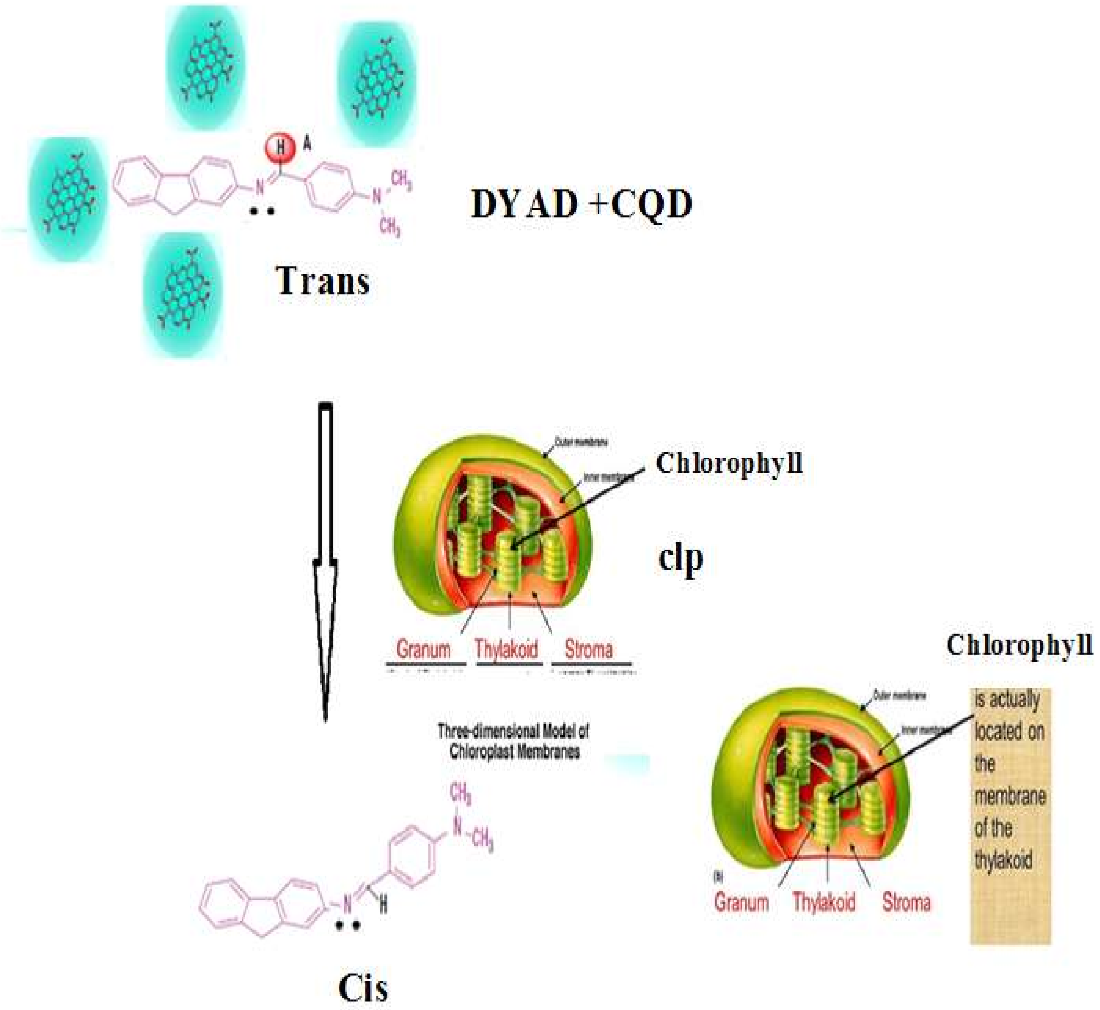

Figure 4.1: Nanocomposits within chloroplast (clp) environment