CHAPTER 1

Optical properties of organic conjugated compounds and nanoclusters

Abstract

The first chapter provides a concise history and advancement of research in the field of photophysical properties of molecules. In this chapter the origin and development of research of several optical properties like luminescence property and nonlinear optical property are briefly described. A special attention is also given to the dye sensitized solar cell with their basic information and working principle. These optical phenomena are conversed on the basis of theoretical approach from the electronic structure theory point of view to realize the structure property relationship.

1.1. Introduction

Human eye is the gift of nature which has the sensitivity to sense electromagnetic waves. The interaction of light with a particular substance defines optical property of that substance. For a long time we have been using this properties to understand the universe and to improve our vision. As for example, one can easily predict the temperature of an incandescent object by the color of emitted light, concentration of a solution can be easily measured by the absorbed light, different colors of light is transmitted by the variation of thickness of a soap film. In the modern civilization scientists are using photons of light to determine materials properties and specialized instrumentation methods are used to expand the range, sensitivity, perception, and precision of our vision, which is known as optical characterization. There are several reports where photons with energies in the range of electromagnetic spectrum have been used for characterization techniques. To develop the photonic components different optical properties such as absorption, refraction, diffraction, scattering, light emission, nonlinear effects, anisotropy, interferences are extensively used. Now a day, in the development of science and technology, optical property becomes the most powerful characterization techniques. As for examples

(i) Blackbody radiation study by Max Planck lead to the formulation of quantum mechanics.
(ii) The discovery and study of the photoelectric effect by Albert Einstein provides evidence of the dual nature of light.
(iii) Optical emission study of atoms and molecules helps to quantize the electron energy levels. The critical observation of emission spectrum of the Sun leads to the discovery of chemical element helium.
(iv) Raman spectroscopy study by C. V. Raman helps to understand the vibrational modes of molecules and used for the identification of a substance.

Optoelectronic properties of organic conjugated molecules and nanoclusters depend on various factors like structure, electronic, morphological and physical properties of that substance. When light falls on a material, electromagnetic field of light interacts with the localized electromagnetic field of atoms. As a consequence of the interaction when light emerges from the material the characteristics and properties may be changed. The interactions depend on the material, field strength and wavelength of the light etc. Inclusion to these different external matters such as temperature, pressure, electric field, magnetic field can also influence the interactions. These interactions are also helpful to fabricate optical devices. In this chapter our intension is to give a brief introduction of two specific optical properties, *viz.*, fluorescence, nonlinear optical properties and dye sensitized solar cell as an application of optical property.

1.2. Luminescence

The word luminescence emerged from Latin term ‘lumen’ which denotes light and here it defines spontaneous emission of light other than incandescence. Actually luminescence is cold-body radiation processes which even occur at normal or lower temperature whereas incandescence is emission of light by a substance as a result of heating. In the luminescence process when a molecule absorbs a photon, an electron is excited from lower energy to higher energy electronic state then the electron again returns to its ground state releasing energy in the form of emission of light. This is known as luminescence. This phenomenon is often observed in nature like *aurora borealis*, luminous animals (glow-worms, fireflies), luminescent wood, rotting fish etc. By using this phenomena researchers are working for the development in the diverse fields like chemistry, biomedical engineering, physics etc.[1]

1.2.1. Classification of luminescence

When incident radiation falls on a material, the material absorbs some energy and some energy is re-emitted in the form of light at higher wavelength. The emitted radiations are found usually in the visible range, also can be found in the UV or infrared region. The wavelength of the emitted light is independent of incident radiation which is the indication of the luminescent substance. This emission is followed by two steps; one is excitation of electrons to higher electronic level and the other is consequent emission of light. The emission of light occurs with significant time gap (τ_c). On the basis of time gap, generally it can be divided into two process, fluorescence ($\tau_c < 10^{-8}$s) and phosphorescence ($\tau_c > 10^{-8}$ s). The fluorescence process is spontaneous and occurs immediately with the absorption of radiation. When the source of excitation is removed this process stops instantly. But in case of phosphorescence it continues for a long time interval even after radiation ceases. Phosphorescence can be further sub-classified into two parts: (a) short period ($\tau_c < 10^{-4}$ s), and (b) long period where $\tau_c > 10^{-4}$ s, also called thermoluminescence (TL). It is found that fluorescence is temperature independent, whereas phosphorescence strongly depends on temperature. The above mentioned process has its own importance and benefit in the field of science and technology.[1] The classification of luminescence phenomenon is shown in Figure 1.2.1.

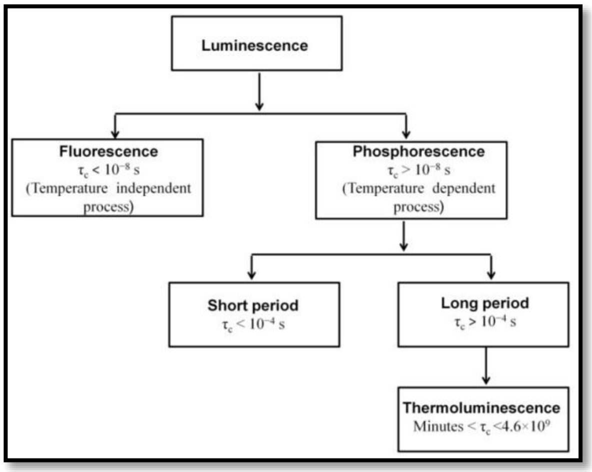


Figure 1.2.1. *Classification of luminescence based on duration of emission.* [1]

1.2.2. Types of luminescence

Luminescence can be categorized according to the different types of source of energy used to excite namely

1.2.2.1 Chemiluminescence: Excitation is done by the energy of chemical reaction.

1.2.2.2 Cathodoluminescence: Excitation is done by a beam of energetic electrons.

1.2.2.3 Bioluminescence: Living organism generates light due to chemical reactions.

1.2.2.4 Triboluminescence: Produced by mechanical energy (e.g. grinding energy).

1.2.2.5 Electroluminescence: Light is produced in response to electric voltage.

1.2.2.6 Photoluminescence: Emission of the light occurs as a result of the excitation by electromagnetic radiation usually by UV radiation.

1.2.2.7 X-ray Luminescence: It is the luminescence activated by X-rays.

1.2.3. Basic principles of luminescence

By using Jablonski energy diagram (Figure 1.2.2) named in honour of the physicist Professor Alexander Jablonski we can demonstrate the luminescence process. Different relaxation mechanisms of the excited state molecules are described here. Jablonski diagram is an energy diagram where energy levels (S_0, S_1, T_1 *etc*) are arranged on a vertical axis and grouped horizontally by spin multiplicity. Due to the vibronic motions of molecules, every energy level consist multiple closely spaced vibronic levels. Each vibrational energy level can be further divided into rotational energy levels. However Jablonski diagram does not include such intense levels. When a molecule is excited, the transition of electron can occur to the first excited state S_1 or second excited state S_2 *etc*. The relaxation can occur in multiple pathways. This process can occur via radiative or nonradiative pathway. Relaxation in radiative way can take place by two mechanisms. 1st one is fluorescence and 2nd one is phosphorescence. Electron in the higher vibronic singlet state S_1 can relax to the lower vibronic state of S_1 by nonradiative transition within picoseconds. If the excited electron is in higher energy singlet excited state (S_2, S_3, S_4, *etc*) it can relax to S_1 state by nonradiative internal conversion (IC) process. Transition between two isoenergetic vibrational levels having different spin multiplicity is known as intersystem crossing (ISC). Triplet states (T_1, T_2, *etc*) are usually populated by ISC process. When transition occurs from singlet excited state (S_1) to singlet ground state (S_0), this emission process is known as fluorescence. This is a radiative spin allowed transition and occurs within a few nanoseconds. Also radiative transitions happen when electron comes down from the lowest triplet vibronic state (T_1) to the ground state (S_0), this emission process is known as phosphorescence. The transition from T_1 to S_0 is much time consuming, ranging from micro- to milliseconds, as it is a spin-forbidden process.[2, 3] It is important to mention that the population of excited triplet and singlet states is dependent on the relative magnitude of rate constant (k_r^S) of the process $S_1 \longrightarrow S_0$ and the rate constant (k_{ISC}) for $S_1 \longrightarrow T_1$ process. Due to spin forbidden formalism the rate constant (k_r^T) of the $T_1 \longrightarrow S_0$ process is normally low.

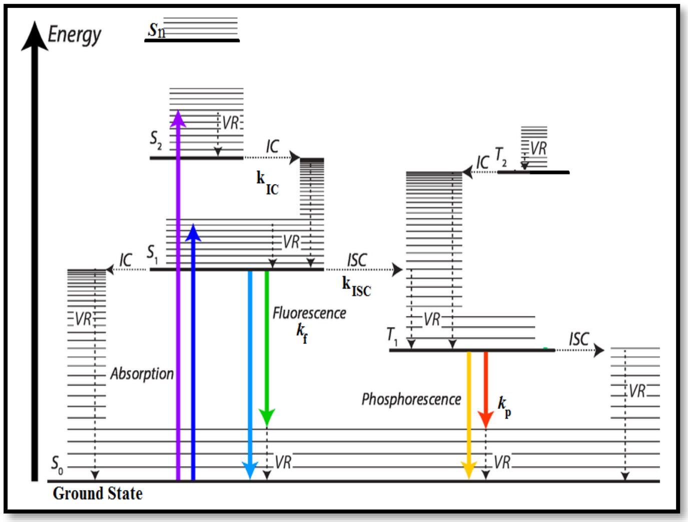


Figure 1.2.2. *Jablonski diagram representing the absorption, fluorescence and phosphorescence.*

1.2.4. Fluorescence

The term fluorescence was given by British scientist sir George G. Stokes in 1852. He demonstrated that when mineral fluorspar was illuminated by ultraviolet radiation it emits red light. He proposed fluorescence as an analytical tool which becomes essential in cell biology, genetics, biomedical sciences and also in materials science due to its high specificity, sensitive emission profiles and spatial resolution. Till now scientists have discovered and developed numerous fluorescent dyes, techniques and applications.

Fluorescence is the characteristics of some atoms or molecules where emitted light has longer wavelength than absorbed light after a short time interval. Three important events occur in the fluorescence process, all events are separated by several orders of magnitude on timescales. A molecule is excited by an incoming photon i.e., excitation occurs in femtoseconds (10^{-15} seconds), whereas picoseconds (10^{-12} seconds) required of excited state electrons to come down at lowest energy level via vibrational relaxation. The ultimate process i.e., returning of the molecule to the ground state takes much longer time of nanoseconds (10^{-9} seconds) via emission of longer wavelength light. Although from excitation to emission complete fluorescence lifetime takes only billionths of a second. The interaction between light and matter in fluorescence process forms the basis for the field of steady state and time-resolved fluorescence spectroscopy and microscopy. Those types of molecules which are capable of endure electronic transitions that finally results fluorescence are known as fluorescent probes or fluorochromes or simply fluorescent dyes. Generally fluorophores are of two types, intrinsic and extrinsic fluorophores. Intrinsic fluorophores are those which occur naturally such as aromatic amino acids, porphyrins, neurotransmitters, green fluorescent protein etc. On the other hand, extrinsic fluorophores are synthesized dyes or modified biochemicals which are added to a substrate to generate fluorescence having particular spectral properties.

1.2.5. Stokes shift and the mirror image rule

Due to the rapid internal conversion from higher excited states to the lowest vibrational energy level the fluorescence emission spectrum does not depends on the excitation energy. It is found that for many fluorophores, the gap between the vibrational energy levels is similar for the ground and excited states, as a consequence, in the fluorescence spectrum a strong resembles of the absorption spectrum occur i.e. mirror image is formed. This is found due to same transitions are most favourable for both absorption and emission spectrum. Therefore, the probability of an excited electron when returns to a particular vibrational energy level in the ground state and the probability of an electron's position in the ground state before excitation are similar, which is known as the mirror image rule. This is demonstrated in Figure 1.2.3. The transition energy related with fluorescence emission is usually less than that of absorption energy, i.e. the photons that emitted have less energy and shifted to longer wavelength region. This incident is known as Stokes Shift.

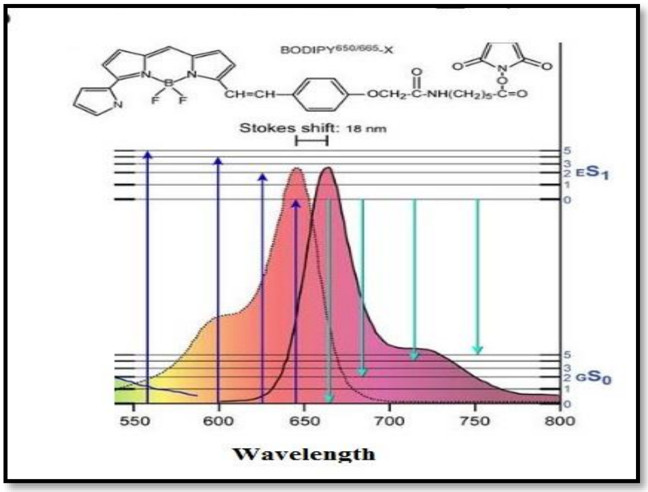


Figure 1.2.3. *Stokes shift and the mirror image rule*[4]

1.2.6. Fluorescence lifetime

Fluorescence lifetime can be defined by the time when a molecule remains in an excited state prior to returning to the ground state. During the excited state lifetime, there are several chances to occur in the fluorophores like conformational changes of fluorophores, interaction with another molecule, and diffusion through the local environment.

The decay of fluorescence intensity is an exponential function of time in a uniform population of molecules when excitation is done with a pulse of light is designated by an exponential function.

$$\mathbf{I(t)} = \mathbf{I_0} \times \mathbf{e}^{\left(-\frac{t}{\tau}\right)} \qquad (1.2.1)$$

Where $\boldsymbol{I}(\mathbf{t})$ defines fluorescence intensity measured at time $\boldsymbol{t}$, $\boldsymbol{I_0}$ is the initial intensity observed immediately after excitation, and $\boldsymbol{\tau}$ defines fluorescence lifetime. The time at which the fluorescence intensity decays to 1/e (approximately 37 percent) of the initial intensity of a fluorescent dyes, can be described as fluorescence lifetime. (Figure 1.2.4) This magnitude is reciprocal of the rate constant for fluorescence decay process from the excited state to the ground state.

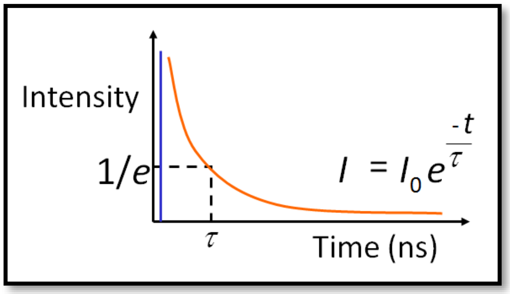


Figure 1.2.4. *Fluorescence lifetime decay profile.*

1.2.7. Solvent effects on fluorescence emission

Several factors like interactions between the fluorophores and surrounding solvent molecules, temperature, pH, other dissolved inorganic and organic compounds, localized concentration of the fluorescent species *etc* can influence the fluorescence emission. The influence of these parameters may vary from one fluorophore to another, although quantum yields, absorption spectra and emission spectra affected heavily by environmental variables. During the excited state lifetime, interactions with the local environment significantly influence the fluorescence process. In the ground state and excited state fluorophores completely behave as a different molecule and exhibits an alternate set of characteristics in association to the interactions with the environment in the excited state compare to the ground state. An ordered distribution of solvent molecules around the fluorophore takes place due to the interaction of dipole moments of both, the surrounding solvent molecules and the ground state fluorophore. The differences between the ground and excited states energy level in the fluorophore create a change in the molecular dipole moment, which eventually induces a re-ordering of the surrounding solvent molecules.

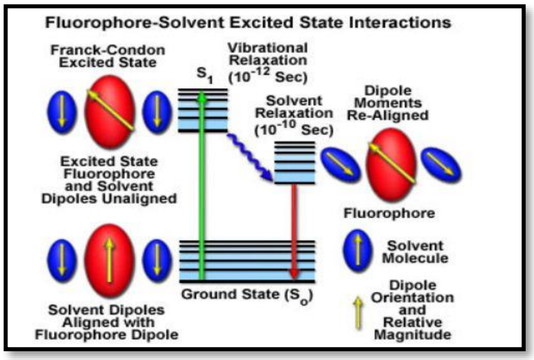


Figure 1.2.5 *Fluorophore-solvent excited state interactions*.

According to the Franck-Condon principle excitation of a fluorophore to a higher electronic energy level occurs in a far shorter timeframe than the fluorophore and solvent molecules in the solvent-solute environment takes time to re-orient themselves. Therefore, between the excitation process and the rearrangement of solvent molecules around the solvated fluorophore there is a time delay demonstrated in Figure 1.2.5. After the excitation process fluorophore reached to higher vibrational energy levels of the first excited singlet state (S_1). Then the excess vibrational energy of fluorophore is transferred to the surrounding solvent molecules and the fluorophore gradually relaxes to the lowest vibrational energy level. Solvent molecules play an important role in stabilization and further reduction of the energy level of the excited state by the solvent relaxation process which is slow process that needs time between 10 to 100 picoseconds. This affects to reduce the energy separation between the ground and excited states, which cause red shift of the fluorescence emission. Larger reduction in the energy level of the excited state occur with increasing the polarity of solvent, while solvent effect on the excited state energy level reduces with decreasing the solvent polarity. It is found that compare to non-polar fluorophores, polar and charged fluorophores reveal a far stronger effect. Stokes shifts in fluorescence are largely influenced by the solvent relaxation. For example, in the tryptophan amino acid heterocyclic indole moiety normally placed on the hydrophobic interior of proteins where the relative polarity of the surrounding medium is low. By the application of heat or a chemical agent, denaturation of a typical host protein occur, therefore the environment of the tryptophan residue is changed from non-polar to highly polar as the indole ring come out into the surrounding aqueous solution. As a result, fluorescence emission is red shifted from 330 nm to 365 nm due to solvent effects. Thus, the solvent polarity plays a key role in the emission spectra of both intrinsic and extrinsic fluorophores.

1.3. Nonlinear optical property

1.3.1. Definition of nonlinear optics

The interactions of applied electromagnetic fields with different materials to generate new field which is different from the incident one altered in phase, amplitude, frequency and other properties are termed as nonlinear optics (NLO).[5] It describes the nature of light in nonlinear media. In nonlinear media the polarization density (**P)** reacts non-linearly to the electric field (**E)** of the light. This kind of nonlinear interactions can only be found with a very high light intensity (electric field) of the incoming field like laser pulse. Figure 1.3.1 represents linear and nonlinear interactions of the wave and the media.

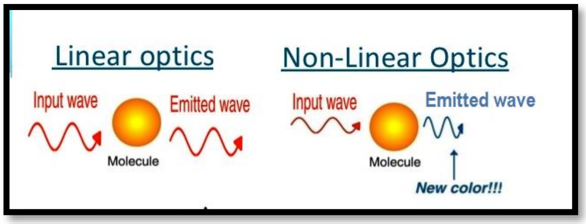


Figure 1.3.1. *Linear and nonlinear interactions of waves and the media.*

In the recent years processing and storage of huge amount of data and information are enormously demanding because of today's social needs. To meet these demands photonics material is one of the optimum choice. Thereby design and synthesis of novel nonlinear optical material have attracted much attention due to their outspread applications associated with optoelectronics[6, 7] and photonics.[8, 9] In Photonics, in order to achieve, accumulate and transmit information, a photon is required instead of an electron. Electronic circuit and photonic circuit have much more similarities. The major dissimilarity found in photonic circuit is photons are conducted through channels and at certain junction points light can be switched from one channel to another. For optical switching we require a material that permits the manipulation of light propagation at these junctions by applying an external electric field or a laser pulse. NLO materials are those which can control the light at these junction points and these are achieving importance day by day in technologies such as telecommunications, optical communication, optical computing, information processing, robotics, dynamic image processing and so on.[10] The major benefit is that photons are much faster than an electron. The photonic circuits are fully compatible with the existing fibre optics networks as it does not interfered by the electrical and magnetic field.[11]

1.3.2. Origin of NLO

To understand the physics in Figure 1.3.1 an energy diagram is considered in Figure 1.3.2. The left part of the diagram indicates the weak beam (non-laser light) interaction with the molecule producing same energy emission as the input light photon energy and hence we get same waves for linear optics. On the right side of the diagram, when a molecule interacts with the high intensity (lasers) light resulting multiple excitation to higher energy level. Therefore emission of light occurs with higher energy than the input light energy. The second one represents nonlinear optics, in which new waves have been generated.

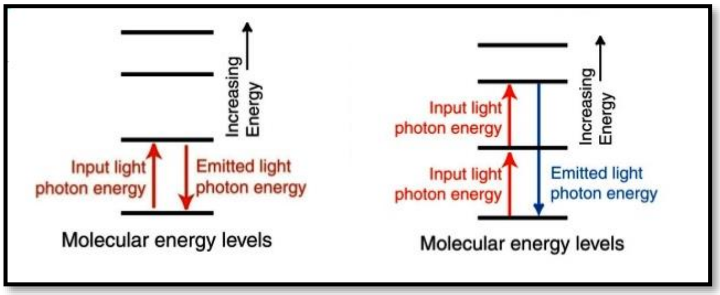


Figure 1.3.2. *Energy band diagram of linear (left) and nonlinear optics (right).*

Different types of polarizations are induced when electromagnetic radiation interacts with a material, depending on their frequency. When low frequency radiation (radiowave and microwave) is used total polarization is contributed by orientation polarization, vibrational polarization and electronic polarization. The first type of polarization indicates reorientation of the molecules; the second type of polarization is connected with the deformation of the nuclear skeleton of the molecule with the applied field. If the radiation wavelength is in the optical range the electronic polarization can occur. For small electric field connected with the electromagnetic radiation, the polarization linearly dependent on the electric field and proportionality constant is known as polarizability (for molecules) and $\chi^{(1)}$ represents the linear electric susceptibility for bulk solids.[12]

$$Polarization = \mu(\omega) = \alpha(\omega).E(\omega)$$

$$P(\omega) = \chi_{ij}(\omega).E(\omega) \qquad (1.3.1)$$

Linear optical materials show this type of response. In the linear response, movement of the charge results reemission of radiation without changing the frequency of the incident light. However the speed of the light may change in induced polarization. This exhibits optical phenomena such as refraction or birefringence. This is due to the fact that the conventional light source has very weak field strength (below 10^3 *v*/cm) compared to the atomic and inter-atomic fields (10^7 to 10^{10} *v*/cm). As a consequence the resultant perturbation is very small to make any change in the optical parameters. But in case of nonlinear optics with discover of lasers the circumstances has changed significantly. There is a scope of resonance as electric field strength of lasers (10^5 - 10^9 *v*/cm) is compatible with the atomic electric fields of the medium. This resonance influences the optical characteristics of the medium and produced new electromagnetic fields where phase, amplitude, and frequency are altered. That's how NLO is produced.[13]

The linear polarization response (given in equation (1.3.1)) does not exist when strong field strength is applied in a medium and the higher order terms become more important. Now the optical response can be illustrated by the following equation where polarization (P) depends on the power series of the field strength (E) as [14]

$$P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \ldots\ldots.. \qquad (1.3.2)$$

$$P = \mu_0 + \alpha E + \beta E^2 + \gamma E^3 + \ldots\ldots\ldots\ldots\ldots. \qquad (1.3.3)$$

The interaction of radiation with bulk material and a molecule are described by equations 1.3.2 and 1.3.3.[15] Here μ_0 represents the permanent dipole moment. Linear optical properties such as absorption, refractive index, permittivity etc are responsible for the linear terms ($\chi^{(1)}$ and α) whereas nonlinear optical properties such as second harmonic generation, electro optic effect, *etc* are responsible for quadratic terms ($\chi^{(2)}$ and β). In this equation cubic nonlinear terms ($\chi^{(3)}$ and γ) are responsible for the third harmonic generation, Kerr effect and optical phase conjugation. Thus fundamental frequency can be converted to the second, third and higher order frequencies by the induced polarization.

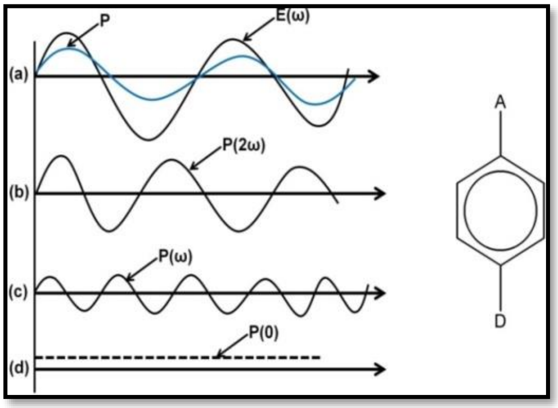


Figure 1.3.3. *(a) Polarization response (P) plot to an incident electromagnetic wave of field strength E(ω) in a noncentrosymmetric medium at frequency ω. (b) to (d) Fourier components of P at frequencies 2ω, ω, and 0.*

This is represented in Figure 1.3.3 for a medium where β (first nonlinear term) provides important contribution to the induced-frequency components. In the figure a non-centrosymmetric molecule is taken for example, which reveals an asymmetric polarization response to the applied electric field *E(ω)*. The polarization of the molecule takes place from electron rich moiety (D) to the electro deficient moiety (A). The polarization nature can be represented by the addition of the Fourier components of frequencies ω, 2ω and 3ω *etc.* (Figure 1.3.3). From the Fourier theorem it is known that a non sinusoidal periodic response (P) is sum of series of sinusoidal functions with harmonics of appropriate coefficients of the elementary frequency (ω). Total polarizability function (P) is expressed by the summation of the even terms (0, 2ω, 4ω, 6ω *etc.*) and the odd terms (ω, 3ω, 5ω *etc.*) for asymmetric and symmetric response accordingly.

A centrosymmetric medium like benzene is taken as an example of a nonlinear response represented in Figure 1.3.4. Here symmetric nonlinear polarization appears from the delocalized π electron system of benzene. The Fourier response decomposition occurs at odd harmonics (*ω, 3ω, 5ω, etc.*) with slowly diminishing amplitudes (coefficients) of the higher order components. In both examples with increment the intensity of the incident field *E(ω)* the nonlinear terms become more considerable.

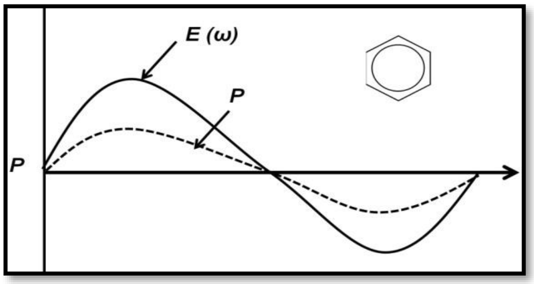


Figure 1.3.4. *Nonlinear polarization response (P) plot to an incident electromagnetic field in a centrosymmetric medium.*

The non-linearity of the optical response of a material is described by the second (β) and third hyperpolarizability (γ). If a molecule is centrosymmetric, then the second hyperpolarizability or first order hyperpolarizability (β) become zero which indicates that centrosymmetric media has no response towards second harmonic generation. This can be interpreted as follows. According to equation (1.3.3) if a field $+E$ is applied to the centrosymmetric medium, the first nonlinear term came out is $+\beta E^2$, whereas when a field of $-E$ is applied, it still comes out as $+\beta E^2$. But this is irrational. The polarization should be $-\beta E^2$ as the medium is centrosymmetric. This disagreement can be resolved only if $\beta=0$.

Thus we can elucidate that the centrosymmetric medium should possess zero β value. In the case of third order NLO susceptibility of centrosymmetric media, the second order hyperpolarizability (γ) is the first non-zero nonlinear term as $+E$ and $-E$ field produces polarization $+\gamma E^3$ and $-\gamma E^3$.[5]

1.3.3. Microscopic nonlinearities

The following equation represents the polarization induced in a molecule with the application of electric field.

$$P_i = \alpha_{ij} E_j + \beta_{ijk} E_{jk} + \gamma_{ijkl} E_{jkl} + \ldots\ldots\ldots\ldots \qquad (1.3.4)$$

i, j, k, l represent the molecular coordinate system and E_j, E_{jk} *and* E_{jkl} etc indicate the components of the applied field. The induced polarization is associated with the electric field vectors through the elements of tensor coefficients in a molecule. Therefore it is a vector quantity. Although in equation (1.3.3) it has been taken as scalar quantity.

The third-rank tensor (β_{ijk}) also has vector like properties, but γ which is a fourth-rank tensor, has scalar like properties. This can be established from the experimental findings where β and γ are related to the components of the tensors which are shown in the following equations.

$$\beta = \beta_{zxx} + \beta_{zyy} + \beta_{zzz} \tag{1.3.5}$$

$$\gamma = \tfrac{1}{5}(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{xxzz} + 2\gamma_{yyzz}) \tag{1.3.6}$$

In order to comprehend the nature of β we take a situation where z-axis is the molecular axis passing through two carbon atoms and donor-acceptor (D-A) groups as represented in Figure 1.3.5. For any arbitrarily chosen field the component will mostly polarize the molecule along the molecular axis (z axis) and β_{zzz} will be the primary component to the nonlinear response. Whereas γ has the scalar properties with field projections contribute in every direction.

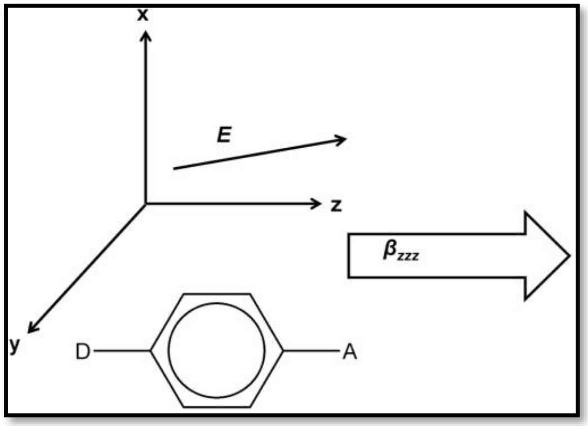


Figure 1.3.5. *Model system with electron donor and electron acceptor substituents which reveals the asymmetric charge distribution along with high β. In the reference coordinate system z-axis is parallel to the dipolar axis of the molecule, the molecule polarized easily along z direction. Here β_{zzz} is the largest component of the β_{ijk} tensor.*

1.3.4. Various types of second-order NLO effects

Different types of second-order NLO effects can be observed experimentally.

1.3.4.1. Second harmonic generation (SHG)

SHG is the most extensive application used in NLO. It is also known as frequency doubling process. In SHG process a nonlinear material is interacted with two photons having same frequency, and then they are combined and produce a new photon having twice the frequency and half the wavelength (double energy) of the initial photons. It is a regarded as sum-frequency generation (2 photons) and more specifically harmonic generation. Lets two photons of frequency v are passed through a medium having characteristics χ^2 and β, the emitted radiation results frequency of $2v$. The incident wave and emitted wave will have the same direction. Figure 1.3.6 pictorially represents the process of SHG.[13]

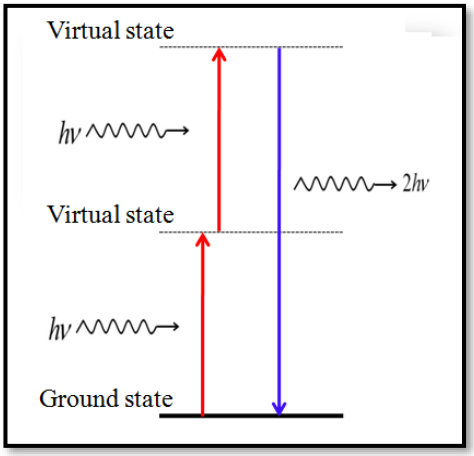


Figure 1.3.6. *Second harmonic generation (SHG)* process.

$$hv + hv = 2hv \qquad (1.3.7)$$

$$\boldsymbol{p_1} + \boldsymbol{p_2} = \boldsymbol{p} \qquad (1.3.8)$$

The p_1 and p_2 represent the momentum of the absorbed photons, and p represents momentum of the emitted photon.

1.3.4.2. Sum frequency generation or parametric generation

It is a second order nonlinear optical process. It is also known as parametric process.[16] In this parametric process two new light waves with frequencies v_1 and v_2 are generated from the light wave with frequency v[17] as shown in Figure 1.3.7. This process generally occurs when the light is interacting with matter, which is asymmetric (for example, surfaces and interfaces) in nature and the light should have very high intensity (Laser pulse). Here the matter remains unchanged and photons satisfy energy conservation rule.

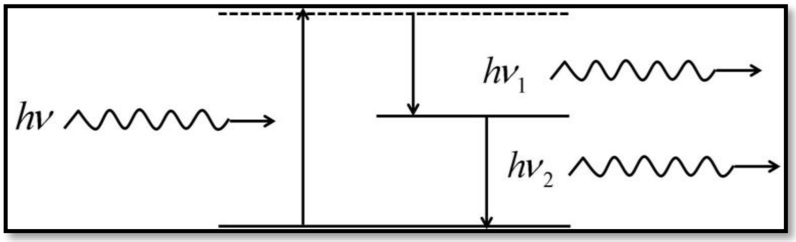


Figure 1.3.7. *Paramagnetic generation.*

$$h\nu = h\nu_1 + h\nu_2 \tag{1.3.9}$$

$$\boldsymbol{p} = \boldsymbol{p_1} + \boldsymbol{p_2} \tag{1.3.10}$$

This process is also illustrated as two-photon process like SHG.

1.3.4.3. Linear electrooptic effect or Pockels effect

In presence of an external electric field, the change of refractive index is proportional to the electric field strength is termed as Pockels effect or linear electrooptic effect. In this case an optical wave is propagated when a DC field is applied through a medium. This effect takes place media such as electric-field poled polymers or glasses. The interacting field components can alter the polarization that modifies the refractive index of the medium.[5]

1.3.4.4. Optical rectification

Optical rectification is also known as electro-optic rectification (EOR), a non-linear optical process. This is an inverse process of the electro-optic effect. When an intense laser beam is directed into the crystal the potentiality to induce a DC voltage between the electrodes placed on the surface of the crystal is defined by optical rectification.[5]

1.3.5. Applications of NLO effects

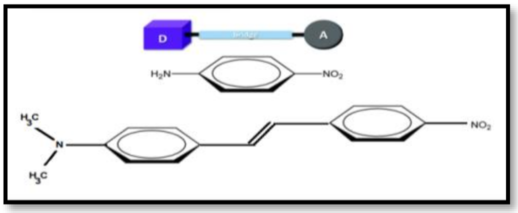
Various frequency and susceptibility dependent applications in various fields for $\chi^{(2)}$ and $\chi^{(3)}$ are represented in the following table.

Table 1.3.1. *Susceptibility functions ($\chi^{(2)}$ and $\chi^{(3)}$) for various types for interacting field components, their effects and applications.*

Susceptibility	Effect	Applications
$\chi^{(2)}(0;\omega,-\omega)$	Optical rectification	Hybrid bistable device[18]
$\chi^{(2)}(-\omega;\omega,0)$	Electro-optic (Pockels) effect	Modulators, variable phase retarders[19]
$\chi^{(2)}(-\omega_c;\omega_a,\omega_b)$	Frequency mixing	Paramateric amplifiers, IR up converters[19]
$\chi^{(2)}(-\omega;\omega;\omega,-\omega)$	AC electro-optic effect AC Kerr effect	Optical bistability [18] Phase conjugation [20]
$\chi^{(2)}(-2\omega;-\omega,\omega)$	Frequency doubling	Harmonic generation device[18]
$\chi^{(2)}(-3\omega;\omega;\omega,\omega)$	Frequency tripling	Deep UV conversion[20]

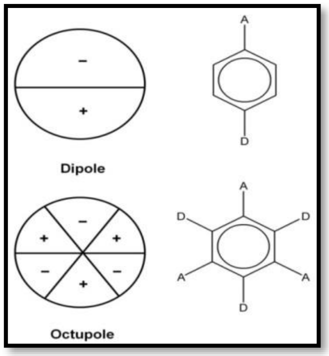
1.3.6. Present status of the field

Non-centosymmetric nature of the material and strong intramolecular charge transfer excitations is the primary requirements of second-order NLO materials as prescribed by theoretical model. *P*-nitroaniline (PNA) (Scheme 1.3.1), dimethylaminonitrisostilbene (DANS) have donor and acceptor group substituents resulting an asymmetric charge distribution satisfy basic criterion for good NLO response.



Scheme 1.3.1. *P-nitroaniline dimethylamino-nitrisostilbene molecules, the prototypical dipolar D-π-A system.*

For the evaluation of NLO properties, DANS has long been considered as typical benchmarking compound due to its well known push–pull character.[5] In this respect, scientists are continuously working on modulation of the electronic structure of the donor-π-acceptor based molecule for producing efficient second-order NLO dipolar molecules. Inclusion to the dipolar molecules, octupolar molecules also show current interest among many research of scientific community in recent times.[21, 22] Due to its multi-polar character multidirectional charge transfer excitations occur which is responsible for NLO response. A prototypical example is shown in Scheme 1.3.2.



Scheme 1.3.2. *Dipolar and octupolar charge distribution in prototypical dipolar and trigonal octupolar systems.*

1.3.6.1. Organic molecules for second-order nonlinear optics

In the early nineties, Marder *et al.* opened the way for the development of advanced NLO chromophores[23, 24] and judicious combination of *D* and *A* groups strengthen the NLO property to maximize $\mu\beta$ for a given conjugation bridge. Conjugated D-π-A based organic molecules reveal significant NLO response and electro-optical effects. This type of materials can be used to enhance frequency of laser light. Usually in D-A substituted organic compounds, D and A are groups are separated by an aromatic spacer. The NLO response of organic molecules can be improved by inclusion of strong electron withdrawing and donating components. The distance between D and A groups also plays significant role. This affects a high charge transfer character in the compound with an asymmetric electron distribution. Internal electric field is generated due to the charge separation in a molecule, which modifies the refractive index through the second-order optical nonlinearity. Theoretical methods are only way to predict first and second order hyperpolarizabilities of organic D-A based compounds. Non-centrosymmetric molecules with high 1st hyperpolarizability value and lowest electronic transitions are very demanding in nonlinear optics. Bond length alteration (BLA) is defined by the average difference between the single and double bond lengths in the molecule which is the key parameter for determining the β of molecules.[25] Generally high β values in a molecule possess high BLA parameter. As for example, compare to simple polyene chain of comparable length, DANS molecule with aromatic ground state have large BLA for a given set of combination of D-A. The high BLA value in such molecules reveals that in the ground state charge separated resonance has very insufficient contribution due to the loss of aromatic stabilization in the charge separated form. Therefore, if a molecule in the ground state possesses less aromatic character, which can be recouped by gain in aromaticity in the charged separated form. When benzene rings are replaced by heterocyclic rings (thiophene, furan etc.) in stilbene derivatives, aromatic character decrease in the ground state and enlaged β value found.[26, 27] Therefore, aromaticity in the charge separated from significantly enhanced nonlinearities in a molecules.[28]

For the design of electro-optic and SHG applications, molecules should have good thermal and chemical stability with high nonlinearities. However, in spite of having high degree of nonlinearity, many organic molecules are thermally unstable. Moylan et al.[29, 30] resolved the matter by replacing the donor groups with diaryl amino groups instead of using aliphatic dialkyl amino group in the chromophore. Hence thermal stability of nonlinear optical material can be enhanced without negotiating the nonlinearity of chromophores.[31,32] Lindsay et al.[33] also demonstrated that by replacing the reactive cyanide group in the tricyanovinyl group with aryl units in tricyanovinyl thiophenes the chemical and thermal stability can be improved significantly. Symmetrical analogues of commercially available 4-(dicyanomethylene-2-methyl-6-94-dimethylamino styryl)-4-pyran (DCM) laser dye is another type of thermally stable compound with good nonlinearity.[33] If dicyanomethylene pyran is used as acceptor and carbazole is used as donors in the above mentioned compound thermally stability can be increased up to 350°C. This molecule has “lambda-shape” structure and is less susceptible to loss of nonlinearities in poled polymer films.[34]

1.3.6.2. Nanocluster complexes for second-order nonlinear optics

In the last few years much attention has been attracted by the nanoparticles, particles with diameter in the range of 1 to 20 nm, due to its versatile applications as they possess distinctive electrical, optical, magnetic and chemical properties which are distinguished corresponding to its bulk material. They are biocompatible and reveal bright emission, therefore can be used as fluorescence bio imaging or cellular labeling. The nanocluster complex can be used for diagnosis, treatment, drug delivery, and for chemotherapy with low side effects.[35, 36]. Optical properties of any materials are ascertained by their electronic structure and band gap. The size and composition of a nanocluster varies with the energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Hence, the optical properties of nanoclusters can be modified by adding different ligands the nanoclusters or with the addition of surfactants. The optical properties of the nanoclusters can be tuned by designing nanoclusters with modified band gaps by simply tuning the size and covering layer of the nanoclusters.[37,38]

Among different properties, nonlinear optical (NLO) response of nanoparticles is a significant phenomenon, which is improved remarkably compared to their relative “bulk” materials, not because of their atomic scale structures but also their surface and interface structures.[39] Electron donating/withdrawing group substituted nanocluster revealed strong dependence on the nonlinear optical property.[40] Different reports specifically enhancement of NLO response of nanocluster doped with alkali metal atoms are also part of valuable literature.[41, 42]

1.4. Photovoltaic property

Photovoltaics (PV) is a phenomenon studied in physics and chemistry where light is converted into electricity using semiconducting materials which demonstrate the photovoltaic effect. This effect is commercially utilized for generation of electricity and photosensors. When natural or artificial light falls on a photovoltaic cell, an electric field is generated across the layers of the materials. The produced free electrons cause electric current which is used to generate electricity. Using photovoltaics, direct current (DC) is produced in solar panels, then the direct current is converted to alternate current (AC) with the purpose of make the electricity usable for home applications. As much as light is absorbed by the photovoltaic material, the more electricity can be generated.

1.4.1. Recent technology: Semiconductor solar cell

In a conventional solid-state semiconductor, a solar cell is made with two types of doped crystals. Crystal is doped with n type and p type impurities. Excess free conduction band electrons are added by n-type impurities i.e. n-type semiconductor and excess holes are added by p-type impurities i.e. by p-type semiconductor. When both semiconductors are placed in contact, some electrons flow into the p-type semiconductor from n-type semiconductor to "fill in" the missing electron holes. At last to equalize the Fermi levels sufficient electrons will flow across the boundary of the two materials. Therefore on both side of the interface i.e. at interface region (p-n junction) charge are depleted and/or accumulated. In silicon a potential barrier is formed due to the transfer of electrons of about 0.6 to 0.7 V.[43]

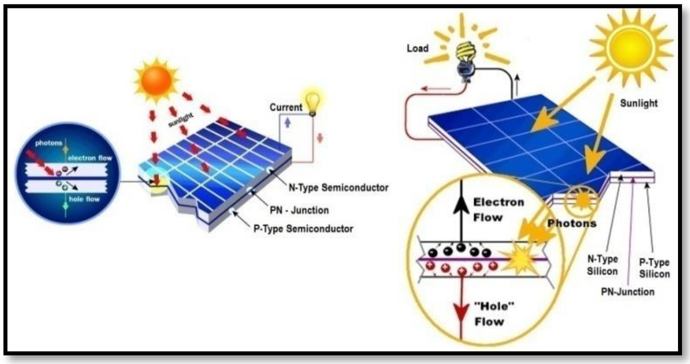


Figure 1.4.1 *Diagram of solar cell.*

When solar cell is placed in the sun, the energy of the incoming photon falling on the surface of silicon material is transferred to the electron of the silicon and allowing the negatively charged electron to move away from the Si atom which leads to the formation of hole or positive charge. Photo-excitation i.e. electrons on the p-type semiconductor is excited by the photons of the sunlight. In case of silicon, sunlight can supply sufficient energy to push an electron out to the higher energy conduction band from the lower-energy valence band. Electrons in the conduction band of silicon can freely move. These free electrons of the p-type side flow out into the n-type side and lose energy while passing through the external circuit when load is given across the cell. Those electrons are flow back again into the p-type material to recombine with the valence band holes which they left behind. By this way sunlight generates an electric current. This is shown in Figure 1.4.1.

1.4.2. Dye sensitized solar cells

The concept behind the DSSC is to imitate the process of photosynthesis in plants. Since the development of the first efficient system in the 1991, the dye sensitized solar cell (DSSC) is regarded as a promising technology due to its high efficiency at a low cost alternative to the Si-based technologies.[44] As this very was first revealed by Grätzel and co-workers; therefore sometimes it is called as Grätzel solar cell.[44,45, 46] DSSCs are thin-film solar cells belonging to the third generation of photovoltaics**.** The solar cell proposed by Grätzel contain a semiconductor anchored with dye molecules and is called the dye-sensitized solar cell. A standard DSSC is made with nano-structured semiconductor generally TiO_2 which is attached with a transparent electrode are covered by dye molecules. The dye molecule absorbed photons from the sun and the excited electrons are transferred by the ultrafast charge transfer process to the semiconductor conduction band and then removed to the external circuit. At the last step the electron is again transferred to the dye from the electrode by an electrolyte. The whole process is illustrated in Fig 1.4.2.

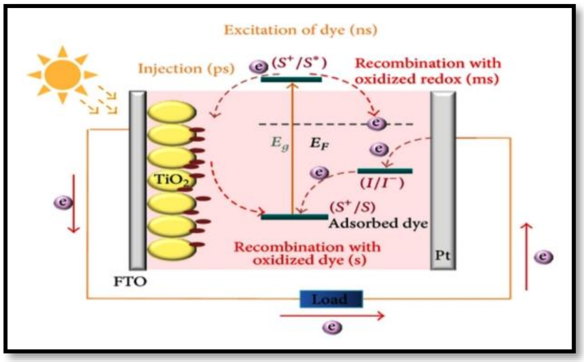


Fig1.4.2. *Construction of the DSSC.*

1.4.3. Titanium dioxide

Titanium dioxide (TiO_2) has versatile application ranges from white pigments in paint to catalyst for water splitting reaction.[47] TiO_2 is chemically very inert in different atmosphere and also stable toward photo-oxidation. As well as it is non toxic, easy and cheap to synthesize. As a result for a model system for the surface science of metal oxides titanium dioxide is a popular choice for both experimental and theoretical chemist.[44] Huge internal surface area of TiO_2 enhanced the light harvesting efficiency by1000 factor and provide a manifold of adsorption sites.[44-46].

In the bulk structure of TiO_2 it is fully coordinated, i.e. it is coordinated with 6-titanium atoms and 3 oxygen atoms. Three major crystalline structures have found in TiO_2: rutile, anatase and brookite. Among them rutile is the most stable. Nano-crystalline TiO_2 films are usually comprised with a mixture of anatase and rutile or anatase. Due to the thermodynamic stability of the anatase structure it is used as electrodes in photovoltaic cells.[45, 48] The high band gap of TiO_2 cause separations of the fully occupied O_{2p} valence band and vacant Ti_{3d} conduction bands. For small nanoparticles the band gap is anticipated to increase, which are used in photo-electrochemical cells. The band gap is 3.4 eV for 2.4 nm anatase nanoparticles. Several theoretical investigations has been done using TiO_2 nanoparticles.[48, 49]

1.4. 4. Dye molecules

The properties and the function of the systems can be extremely modified by the adsorption of different molecules on TiO_2 surface. Many investigations on the small molecules anchored to the surfaces of the TiO_2 have been done due to research interests, especially with hydrogen, oxygen, and water as adsorbates.[47, 50, 51] The interaction between small and large adsorbates and surfaces are very significant due to large number of applications. Adsorption of dye molecules on the semiconductor surfaces can extend their effectiveness towards photochemical applications.

1.4.5. Electronic and optical properties of isolated dyes

A number of conditions must be satisfied in order to achieve a high DSSC efficiency like; (i) broad absorption spectrum with large overlap with the solar spectrum (wavelength of light in the 400 – 750 nm range) , (ii) high molar extinction coefficient, (iii) strong anchoring group for the interaction with semiconductor electrode, (iv) appropriate redox potential to match electron injection, (v) HOMO of the dye must have low energy than the redox potential of the electrolyte and LUMO of the dye must lie above the conduction band of semiconductor. (vi) the electron transfer from the excited dye to semiconductor surface should be very fast to the reduction of the oxidized dye.[52-55] Inclusion to these criteria, the back reaction from semiconductor to oxidized dye must be slow, level alignment criterion, the regeneration of the oxidized dyes by the electrolyte, losses due to charge transport and recombination process etc also influences the efficiency of DSSC.

1.4.6. Organic dyes

Organic (metal-free) dyes are important class of chromophores in DSSC as they possess several advantages like ease of availability, cost effectiveness of synthesis, tunable absorption spectra from the visible to the near-infrared region, designing flexibility, high molar extinction coefficients etc.[54, 56, 57] Very common organic chromophores proposed in DSSC are coumarin, indoline, triphenylamine, xanthene, polyene, hemicyanine-based dyes.[58] The efficiency of dyes in the DSSC devices continuously increasing over the past few years.[58-60] Although there are some limitations of organic dyes including narrow absorption bands, poor photostability and aggregation in solution. Many of the organic dye sensitizers consists donor-π-linker-acceptor (D-π-A) framework. These types of chromophores contain π-conjugated bridge which is end-capped by donor (D) and acceptor (A) groups. Generally Triphenylamine or indoline group is used as electron donor; rhodamine or cyanoacrylic group is used as electron acceptor as well as an anchoring group for binding to the semiconductor surface; and π-conjugated fragment (e.g. ethylene, azo group, benzene, thiophene units etc) control the absorption properties, provide a route for the ultrafast rearrangement of electric charges, enhance the molar extinction coefficient etc. The HOMO of the dye molecule is mainly localized on the donor part, and LUMO is delocalized on the acceptor part. The lowest-energy excitation in organic dyes are mainly associate with the π-π* transition. Due to photoexcitation charge transfer takes place from the D to A moiety of the molecule. The photoexcited dye can be represented as $(D^+\text{-}\pi\text{-}A^-)^*$. Such structure has several advantages: (i) As LUMO is localized near the semiconductor surface electron injection from dye to semiconductor is fast (ii) As the donor part is away from the semiconductor, inhibits recombination process and prevents the positive charge of the oxidized dye away from the semiconductor.

1.4.7. Present status of the field

Two major types of sensitizers commonly used as metal complexes and metal-free organic dyes. Highest performance DSSCs with power conversion efficiency (PCE) exceeding 11.8% is shown by N719 Ru(II)-polypyridyl photosensitizers[61], in the year 2011 the best PCE of DSSCs up to 12.3% is found for zinc porphyrin-based dye[62] After two year a solid-state DSSCs PCE exceeding 15% PCE was independently developed by Gratzel and Oxford University research teams which further make a new record.[63, 64] Using pure organic sensitizer (C281) attainment of PCE 13.1% in DSSCs has been achieved with a metal-free organic dye.[65] Kar et al. in 2017 reported PCE of DSSCs in 19.24%. using N,N′-dialkylaniline (NDI 6).[66] Organic dyes for examples coumarin,[67] triphenylamine (TPA),[68] polyene,[69] phenothiazine,[70] indoline[71] etc have been investigated for DSSCs which reveal good photovoltaic property.

1.5. Aim of the present work

For designing potential optoelectronic materials, computational modeling is an efficient tool. Computational modeling helps to eliminate the high costs associated with the synthetic approach. This offers the synthetic chemists to get immediate feedback of compounds for potential use. It is found that various optical properties calculated theoretically using different methodologies show good agreement with the experimentally calculated optical properties. Therefore before synthesizing a molecule, computational methodology is now accepted as a state-of-the-art technique in modeling the potential molecules. Keeping in mind the achievement of quantum chemical methods in prediction of different optoelectronic properties, the thesis distinctively deals with the computational modeling of optoelectronic materials as given below:

(1) Electron donating and electron withdrawing groups can significantly tune the optoelectronic properties of organic chromophores, attempts have been put in order to design efficient fluorophore molecule based on organic conjugated molecules.

(2) Photovoltaic materials with interesting nonlinear optical properties (NLO) are of enormous importance due to their versatile applicability in photonic devices. Different electron withdrawing groups and π-linkers could considerably enhance the NLO properties of organic conjugated dyes. A great deal of attention has been given to the photovoltaic properties of dye sensitized Solar cell (DSSC) of organic conjugated molecules as these systems have potential application in photophysical chemistry.

(3) Intramolecular charge transfer process can play a key role in developing strong nonlinear optical response in a molecule for technological application. Push–pull systems with zwitterionic donor–acceptor groups can enhance the hyperpolarizability values drastically compared to the neutral substituents. Therefore, attempts have been put in order to designed novel NLO materials which show characteristic reorganisation energy is a deciding factor in the rate of hole/electron transport for favourable intermolecular coupling. π-conjugated linkers and electron acceptor groups can be judiciously used to design new molecular systems for optoelectronic applications.

(4) Focus of the present research has shifted from organic conjugated molecules to donor-acceptor (D-A) groups functionalized nanocluster systems. Functionalization of D-A groups lead to an extremely large 1st hyperpolarizability. The significant hyperpolarizability in donor-acceptor groups functionalized nanocluster arises due to charge transfer from D to A moiety. Here we have showed that the right choice of substitution can considerably impact the nonlinear optical property of the nanoclusters.

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