Introduction

1.1. Electron donor-acceptor (EDA) based systems

Electron transfer (ET) processes are vital in various fields like physics, chemistry, and biology. Generally, ET involves the transfer of electrons from one system to another. Such a process occurs due to the attendance of an electron-rich donor (**D**) and an electron-deficient acceptor (**A**) unit. Using this phenomenon, various chromophoric systems are designed by comprising different electron **D**-**A** units, sometimes termed an EDA system. These systems have various photophysical features, which can be easily tuned by changing the strength of "**D**" and "**A**" units for desired applications. However, EDA-based chromophoric systems have various applications in materials, organic, and medicinal chemistry. In the subsequent sections, all the characteristics and photophysical features of EDA systems are discussed in detail.

1.2. Characteristics of EDA-based systems

EDA-based systems involve molecules or compounds that can donate or accept electrons. The electron "**D"** is typically a molecule with a higher energy level of electrons than the "**A**", which makes it more likely to donate an electron. In contrast, the "**A**" has lower energy level of electrons, which makes it more likely to accept an electron. The transfer of electrons from the "**D**" to the "**A**" leads to the development of EDA systems.

The strength of the interaction between the "**D**" and "**A**" molecules depends on several factors, including their molecular structures, electronic features, and the solvent used. For instance, the capacity of the interaction between the "**D**" and "**A**" molecules rises with the overlap of their molecular orbitals. The presence of electron-donating group (EDG) or electron-withdrawing group (EWG) on the "**D**" or "**A**" molecules can also influence the strength of the EDA interaction. Solvent polarity can also affect the EDA interaction by stabilizing or destabilizing the EDA systems.

One of the key advantages of EDA systems is their tunability. By varying the chemical structure of the "**D**" and "**A**" units, it is possible to control the energy levels of the excited state complex and optimize the efficiency of the ET process. This has led to the progress of an extensive range of EDA systems with unique features and potential applications. For example, EDA systems have been used to develop organic solar cells, which convert sun illumination into electricity [1–4]. In these systems, a "**D**" molecule, such as a conjugated polymer, is paired with an "**A**" molecule, such as fullerene. When illumination is absorbed, electrons are excited from the "**D**" to the "**A**", resulting in the development of an excited state complex that can be used to generate a photocurrent.

EDA systems have also been used in the development of molecular sensors. In these systems, the "**D**" and "**A**" molecules are designed to respond to specific analytes, such as metal ions or biomolecules. When the analyte binds to the "**D**" or "**A**" molecule, the energy levels of the excited state complex are altered, resulting in an alteration in the fluorescence or UV-visible spectra of the system. This can be used to detect the presence or concentration of the analyte to a given sample.

However, chemosensors or molecular sensors based on EDA systems could selectively bind a certain receptor and analyte under crowding condition, and it may convert compatible signals from receptor analyte interactions into optical or electrochemical signals. Optical techniques are more appropriate since it transform chemical input into various optical outputs, including absorbance, fluorescence, phosphorescence, refractive index, etc. Furthermore, the low cost, straightforward apparatus, and ability to visually identify the target analyte up to low concentrations make these procedures superior to older ones. Therefore, recent advances in supramolecular chemistry have enabled the fabrication of fluorescent or colorimetric chemosensors that exhibit discrimination for a particular analyte in crowding situations [5,6]. This Ph.D. thesis's entire body of work will be able to deliver a comprehensive summary for the designing of EDA-based chemosensors that can detect a variety of physiologically significant analytes, including acid-base, cations, anions, nitro explosives, and nerve agent mimics, with extreme sensitivity and selectivity. The EDA system and chemosensors based on it are briefly described in this chapter before going on to a study of the general concept and mechanism underlying the designing of EDA-based chemosensors on behalf of various photophysical processes.

1.2.1. Chemosensor

A chemosensor is a chemical sensor that can detect and measure the concentration of a specific target analyte. Chemically, it is an EDA molecule or material that can collaborate especially with a specific analyte, causing a confined physical alteration such as absorbance, fluorescence, or electrical conductivity [7]. It might be as little as a glucose detector, pH electrode, or even a single molecule to distinguish a specimen from a certain environment. Examples include the dyes phenolphthalein and methyl orange. As a result, it is feasible to conclude that a chemical event and the sensors in EDA systems are closely coupled. The following functions may be followed by a specific-assemble chemosensor: (a) When there are many analytes present at once, it interacts with one of them in a specific and unique way. (b) operational outcomes reports serve as an analytical signal that aids in qualitative and quantitative analysis, and (c) when used in biological applications, chemosensors must be stable and non-toxic in the biological pH range [8].

Chemosensors based on EDA systems are a common type of chemosensor. The basic parts of an EDA chemosensor include:

(a) Electron "**D**": This chemical group or molecule can donate electrons to the EDA system when interacting with an analyte. Examples of electron "**D**" groups include amines, phenols, and thiols.

(b) Electron "**A**": This chemical group or molecule can accept electrons from the EDA system when interacting with an analyte. Examples of electron "**A**" groups include nitro groups, carbonyl groups, and metal ions.

(c) Linker: The electron "**D**" and "**A**" groups are connected by a linker that allows the EDA system to respond to environmental alterations. The linker may be a simple carbon chain or a more complex molecule, depending on the application.

(d) Analyte: The analyte is the target chemical compound or molecule that the chemosensor is designed to detect. The electron "**D**" and "**A**" groups of the EDA system selectively interact with the analyte, causing a variation in the physical or chemical features of the system.

Overall, the EDA system-based chemosensor can retaliate to variations in the electronic context caused by the attendance of the analyte. This can lead to a confined alteration in a property of the system, such as fluorescence, color, or electrical conductivity, which can be used to detect and quantify the analyte [9,10,11]. **Figure-1.1** illustrates the interaction of the **D**-**A** chemosensor with the binding of the analyte.

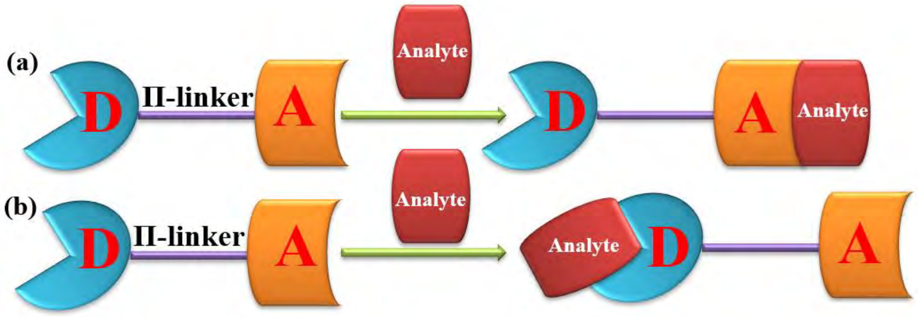

Figure-1.1. Schematic demonstration of chemosensor **(a)** interaction of **"A"** with analyte; **(b)** interaction of **"D"** with analyte.

1.2.2. Optical sensors

An optical sensor is a tool that uses illumination to detect and measure physical phenomena, such as the presence or absence of an object, the distance to an object, or the level of a particular substance. Optical sensors work by converting alterations in illumination into electrical signals, which a computer or other electronic device can process.

Optical sensors are designed to detect and measure the photophysical features of illumination. These features include:

(a) UV-visible: Optical sensors can detect the amount of light absorbed by a sample. This property is used in applications such as spectrophotometry, which measures the concentration of a substance in a solution.

(b) Fluorescence: Optical sensors can detect fluorescence, which is the fluorescence of illumination by a molecule after it has been excited by the radiation of a shorter wavelength. Fluorescence can be used in applications such as fluorescent microscopy, which is used to study biological samples.

(c) Refractive index: Optical sensors can detect alterations in the refractive index of a sample. This property is used in applications such as biosensors, where it can be used to sense the binding of a biomolecule to a sensor surface.

(d) Polarization: Optical sensors can detect alterations in the polarization of light. This property is used in applications such as polarimetry, which is used to study the structure of biological molecules.

Various optical sensors, including photodiodes, phototransistors, and photomultiplier tubes, can detect the photophysical features of illumination. These sensors are often combined with optics, such as filters and lenses, to enhance their sensitivity and selectivity [12]. As a result, optical sensors outperform supplementary outmoded sensors concerning features, including selectivity, sensitivity, and a wide variety of wavelengths. As a result, there are two distinct categories for optical sensors.

1.2.2.1. Colorimetric chemosensor

In sensor research fields for physiological and ecological applications, the introduction of colorimetric chemosensors is an active, vital element of many chemical species that may be cations, anions, or neutral species. As far as colorimetric chemosensors are concerned, they exhibit a discernible colorimetric alteration through the signaling unit due to their strong affinity for the target analyte and a particular coordination mode of the sensor. A colorimetric sensor has several benefits in sensor research, including being very selective and sensitive, directly detecting colorimetric alteration, being cost-effective, and avoiding using complicated apparatus [13]. As a result, such colorimetric chemosensors are expanding in several applications, such as biological and environmental monitoring and medical diagnostics [14,15]. Most colorimetric sensors exertion in the visible range of radiation, and different photoactive chemicals are used to identify analytes [16], and it quickly became clear that the mainstream of them have a system of alternative π-bonds; as a result, it was crucial to identify the dye's type by associating the energies of the HOMO and LUMO. However, it was closely associated with the increased redshift (bathochromic shift) in the UV-visible spectrum that reduced energy divergence among the ground and excited states of molecules [17]. The two factors EDG, such as -NH_2, -NHR, -NR_2, -OH, -OMe, etc., and EWG, such as -NO_2, -COOH, -CN, -SO_3H, C=O, etc. often determine the UV-visible spectra of a conjugated molecule. A charged transfer band is seen in the UV-visible spectra when an organic molecule conjugates the two groups.

The EDA system is commonly created in chemosensors by appropriately positioning EDG and EWGs. A metal ion's capacity to donate electrons is diminished when it attaches to the EDG, varying the **D**--**A** system into an **A**--**A** system with decreased conjugation. As a result, the UV-visible spectra shift to the blue, and the possibility of LMCT rises [18–20]. Alternatively, when a metal ion binds to the EWG, it reinforces the **D**-**A** system and increases the possibility that MLCT will manifest. [21]. As a result, the ground state is less stable than the excited state, which causes the UV-visible spectra to shift toward the red. **Figure-1.2** illustrates this phenomenon.

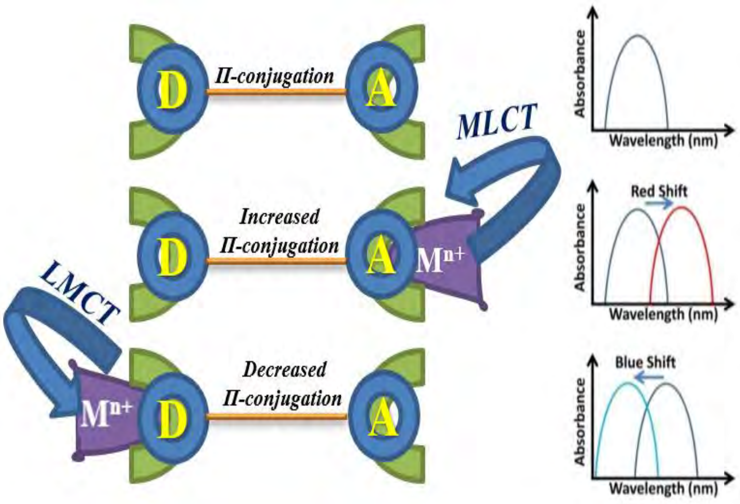

Figure-1.2. Illustrative demonstration of the effect of binding of cation on **D**-π-**A** system and the UV-visible spectrum.

1.2.2.2. Fluorescent chemosensor

An EDA-based fluorescent chemosensor is a type of fluorescence chemosensor that utilizes a **D-A** system to detect the existence of specific chemicals or ions in a sample [22]. The **D-A** system comprises a fluorescent "**D**" molecule and a non-fluorescent "**A**" molecule connected through a chemical linker. When the "**D**" and "**A**" are brought into proximity, energy is transferred from the excited "**D**" to the "**A**", causing the fluorescence of the "**D**" to decrease or completely quench.

When the **D-A** system interacts with a target chemical or ion, the linker between the "**D**" and "**A**" alters its structure or conformation, leading to a disturbance of the energy transfer (Et) process and a recovery of fluorescence. This alteration in fluorescence can be measured and used to govern the concentration or presence of the target chemical or ion.

These have been used to sense various chemicals, including metal ions, organic compounds, and biological molecules. These are highly selective and sensitive, with nanomolar or even picomolar range detection limits. Additionally, the **D-A** system can be modified to fine-tune the features of the chemosensor, such as its sensitivity and selectivity, making it a multipurpose means for various uses in chemistry, biology, and environmental monitoring affordable technology [23–26].

1.2.2.2.1. Principles for designing fluorescence chemosensors

A sensor produces a measurable form of energy when it detects an analyte. This is called signal transduction. Fluorescence is an ideal signal transduction mechanism for sensing applications because it has a high sensitivity. It emits light at a longer wavelength than it absorbs, requiring low analyte concentrations ($>10^{-6}$ M) to create a strong signal.

One of the most widely used techniques for sensing applications is luminescence, especially fluorescence because it offers many advantages, such as flexibility, real-time capability, and suitability for low sensor concentrations. Moreover, fluorescence detection can be done with low-cost instruments. A fluorescent sensor is a molecular device that can signal the presence of an analyte, such as ions and molecules. A fluorescent sensor consists of two main components: a receptor and a fluorophore, as shown in **Figure-1.3**. The receptor is responsible for recognizing the analyte, while the fluorophore is responsible for producing an optical response by transforming the recognition event into a signal.

As shown in **Figure-1.3**, the receptor selectively and efficiently binds to the analyte. Various factors affect the success of this binding, such as the shape of the ligand, the properties of the target ion or molecule (such as ionic radius, charge, coordination number, hardness, etc.), or the structure of organic molecules, including drug candidates. The solvent’s nature, including pH, ionic strength, and polarity, is also important to consider, as it can greatly affect the receptor’s recognition and binding of the analyte.

Fluorescent sensors can also be designed to detect multiple analytes or combinations of different analytes within a given sample. In the case of fluorescent sensing, there must be an active communication pathway between the signaling and recognition moieties. The recognition of an analyte at the receptor side induces a modulation in the photophysical properties of the fluorophore.

The fluorescent sensor should have thermal and photochemical stability, and the sensor-analyte binding should be reversible to allow continuous analyte monitoring. For this reason, most sensors are made of simple structures where a chemical bond or a covalent spacer connects the fluorophore and the receptor. Alternatively, they may be incorporated in the same structure, ensuring a functional communication pathway, as illustrated in **Figure-1.4a** and **Figure-1.4b**.

Fluorescence can detect very small changes, even at the molecular level. Although most sensing applications do not require single-molecule detection with commercial spectrometers, changes in fluorescence emission wavelength (λ_{max} or λ_{Flu}), fluorescence quantum yield (ϕ_F), and lifetimes (τ) are used to measure and quantify the strength and affinity (binding constants) of the host-guest interaction during sensing events. Changes in fluorescence excitation spectra and polarization can also be useful for sensing applications. The next section will discuss various photophysical processes, focusing on those designed for charged species and the principles used in their development. Selective examples of how sensor design principles affect the photophysical properties of the sensors will be presented, including the use of integrated receptor-fluorophore systems [27–29] (**Figure-1.4b**).

Figure-1.3. A diagram illustrating a sensor that undergoes alterations in its photophysical properties upon detecting an analyte.

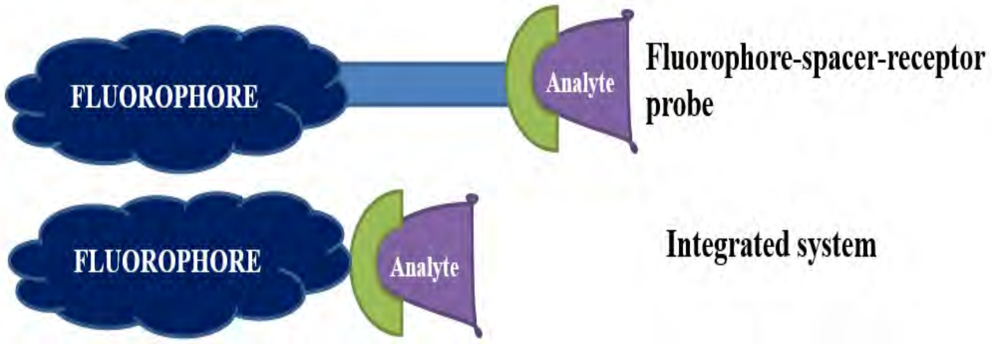

Figure-1.4. Schematic depiction of binding of the fluorophore.

1.2.2.3. Signalling mechanisms for chemosensor

The search for innovative sensing mechanisms that may be employed to create inventive chemosensors is now of attention. Different conventional signaling mechanisms have been created based on photophysical processes, including excimer/exciplex formation, AIE, C=N isomerization, and ESIPT. These processes comprise PET, ICT, MLCT, TICT, and FRET. These techniques permit communication between signal reporting units and recognition systems. A couple of these processes are discussed in more detail below.

1.2.2.3.1. Photoinduced electron transfer (PET) process

The PET method can be defined in EDA systems concerning the energy transformation between the HOMO and LUMO of the "**D**" and "**A**" molecules. When a photon is absorbed by the "**D**" molecule, an electron in the HOMO is excited to the LUMO. Suppose the energy transformation among the HOMO and LUMO of the "**A**" is lower than the energy transformation among the HOMO and LUMO of the excited "**D**". In that case, the excited electron can transfer to the "**A**" molecule. This forms a charge-separated state, where the "**D**" is oxidized and the "**A**" is reduced [30]. The rate of the PET method is determined by the overlap between the "**D**" LUMO and the "**A**" HOMO. The closer the energy levels of the LUMO and HOMO are, the faster the PET process will occur [31,32].

The equation can describe the PET process:

$$\mathbf{D^* + A \rightarrow D^+ + A^-}$$

Where "**D***" represents the excited state of the "**D**" molecule and "**A**" represents the acceptor molecule. The resulting charge-separated state can be detected through various mechanisms, including fluorescence quenching, alterations in UV-visible, or electrochemistry. In the absence of PET, the chromophore gives high luminosity (**Figure-1.5**) [33]. When the LUMO of the fluorophore is sandwiched among the HOMO and LUMO levels of the analyte-integrated receptor, a non-radiative way for quenching luminosity is observed (**Figure-1.6**). Therefore, there are two types of PET process: Turn-On PET and Turn-Off PET. Turn-On PET fluorescence sensors involve the HOMO and LUMO states of the fluorophore as well as the HOMO level of the bar receptor (formerly analyte attachment), while the Turn-Off fluorescence sensors, in contrast, use the HOMO and LUMO states of the fluorophore and the LUMO level of the analyte subsequently complex formation.

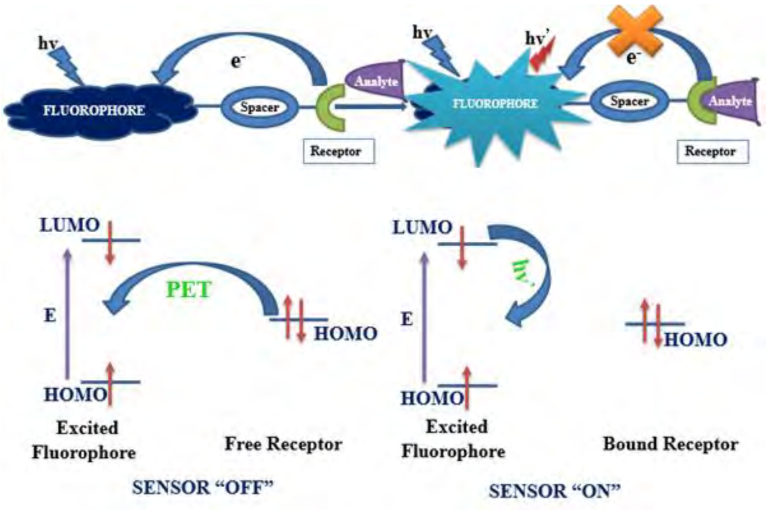

Figure-1.5. The PET process is depicted schematically.

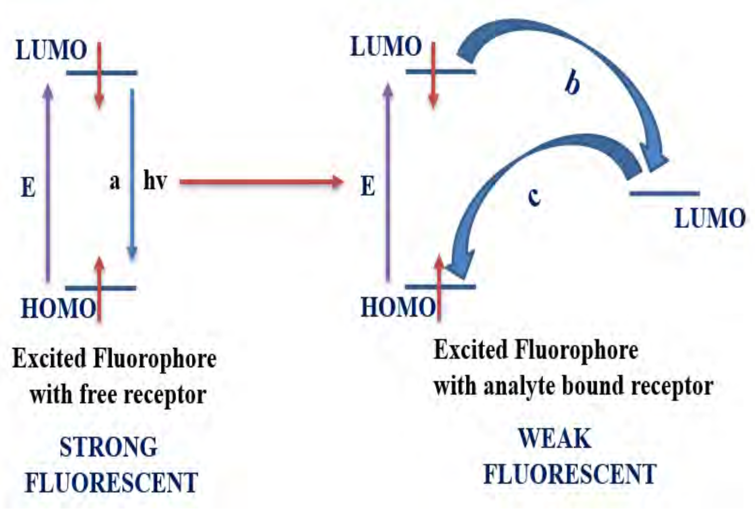

Figure-1.6. Schematic illustration of reductive PET.

1.2.2.3.2. Intramolecular charge transfer (ICT) process

ICT is a type of PET that occurs within a single molecule, where the electron is transferred from the "**D**" moiety to the "**A**" moiety inside the same molecule. In an EDA system, the presence of an ICT state is governed by the relative energy levels of the HOMO and LUMO of the "**D**" and "**A**" moieties. In an ideal **D**-**A** system, the HOMO of the "**D**" is lower in energy than the LUMO of the "**A**", allowing for efficient PET between the two moieties. However, the HOMO-LUMO energy gap is insignificant. In that case, an excited state can be formed within the molecule where the electron is partially transferred from the "**D**" to the "**A**" moiety. This creates an ICT state where the electron density is spread over the "**D**" and "**A**" moieties [30,34,35]. However, the extent of the ICT state can be modulated by the substituents on the "**D**" and "**A**" moieties and the molecular geometry. For example, increasing the electron density on the "**D**" moiety or decreasing the electron density on the "**A**" moiety can increase the ICT character. This results in a shift in the molecule's UV-visible and fluorescence spectra (**Figure-1.7**) and alterations in other photophysical and photochemical features. Moreover, ICT in **D**-**A** systems has utilities in designing chromo-fluorogenic chemosensors, where the formation of an ICT state upon binding to the target analyte leads to an alteration in the photophysical features of the molecule, allowing for the detection of the analyte. ICT can also be used to design organic materials for electronic devices such as solar cells, where forming an ICT state upon UV-visible illumination can lead to efficient charge separation and energy conversion.

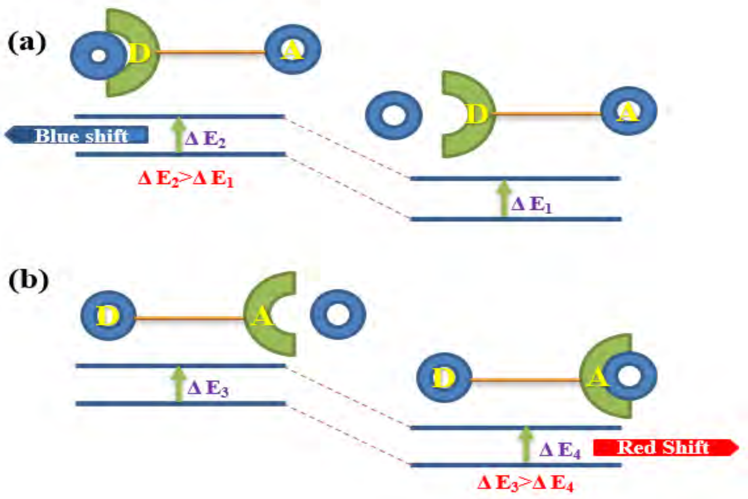

Figure-1.7. Fluorescent ICT sensors are used in **(a)** cation recognition (interaction with the "**D**" group) and **(b)** cation recognition (interaction with the "**A**" group).

1.2.2.3.3. Quenching of fluorescence

The quenching of fluorescence in EDA systems can arise through dynamic and static quenching. Dynamic quenching involves collisional interactions between the fluorophore and the quencher, where the excited state energy of the fluorophore is shifted to the quencher through non-radiative processes, such as ET or energy transfer. In EDA systems, the ET process is usually responsible for dynamic quenching. When the electron "**D**" and "**A**" are in proximity, the excited state energy of the "**D**" can be shifted to the "**A**" through ET, resulting in the reduction in the fluorescence intensity of the "**D**". However, static quenching, on the other hand, occurs when the fluorophore and the quencher form a non-fluorescent complex. In EDA systems, the complex formation can occur when the "**D**" and "**A**" bind together, establishing a non-fluorescent ground-state complex. As a result, the fluorescence intensity of the "**D**" is quenched. Both dynamic and static quenching can contribute to the quenching of fluorescence in EDA systems, depending on the precise experimental circumstances and the nature of the "**D**" and "**A**" molecules involved.

The transition metal ions, such as Fe^{3+}, Cu^{2+}, Co^{2+}, Ni^{2+}, etc., transfer energy and electrons to the fluorophore because of those metal ions' suitable vacant or half-filled d-orbitals energy. Thus, fluorescence quenching can occur [36]. As shown in **Figure-1.8**, the robust interaction between the partially occupied electron of the metal ion and the electrons of the fluorophore is responsible for this intriguing association observed in numerous metal complexes. This interaction facilitates the ISC process, allowing the energy transfer from the singlet excited states of the fluorophore to states with greater multiplicity [37].

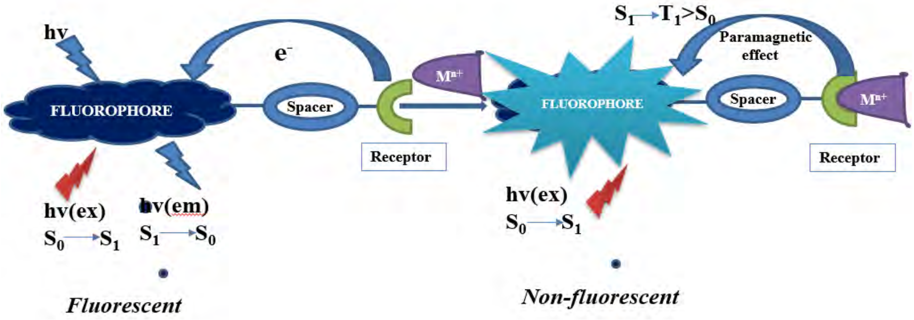

Figure-1.8. Schematic diagram showing paramagnetic fluorescence quenching.

1.2.2.3.4. Forster resonance energy transfer (FRET)

FRET is a mechanism for energy transmission among two chromophores, typically a **"D"** and an "**A**", that is close. FRET occurs when the photoluminescence spectrum of the **"D"** overlaps with the UV-visible spectrum of the "**A**" and when the distance between the two chromophores is within a certain range (typically less than 10 nanometers). In EDA systems, FRET can occur when a "**D**" and an "**A**" are close, and the Et occurs through the dipole-dipole interaction between them [38,39]. In a FRET process, the "**D**" chromophore absorbs a photon and becomes excited. The excited "**D**" can transfer its energy to the "**A**" chromophore through a dissipative process, such as dipole-dipole interaction or resonant Et. The ET occurs without fluorescence of a photon by the "**D**" chromophore. Instead, the "**A**" chromophore is excited, and it releases a photon with an extensive wavelength than the "**D**". The efficiency of FRET relies on several factors, including the distance between the "**D**" and "**A**", the spectral overlap among the "**D**" fluorescence and "**A**" UV-visible spectra, the relative orientation of the "**D**" and "**A**" dipoles, and the quantum yield of the "**D**" [40].

In EDA systems, FRET is a useful tool for probing molecular interactions and distances, as it can provide information about the energy transfer efficiency and the distance among the "**D**" and "**A**" molecules. FRET has many applications, including imaging, biosensing, and energy harvesting systems. However, the separation between the two fluorophores in FRET can be impacted by the existence of metal ions. The fluorophores can move closer or further apart when metal ions connect. The FRET mechanism is improved when the metal ion brings the two fluorophores closer, resulting in a smaller gap between them. The impact of metal ions on FRET is seen in **Figure I.9**.

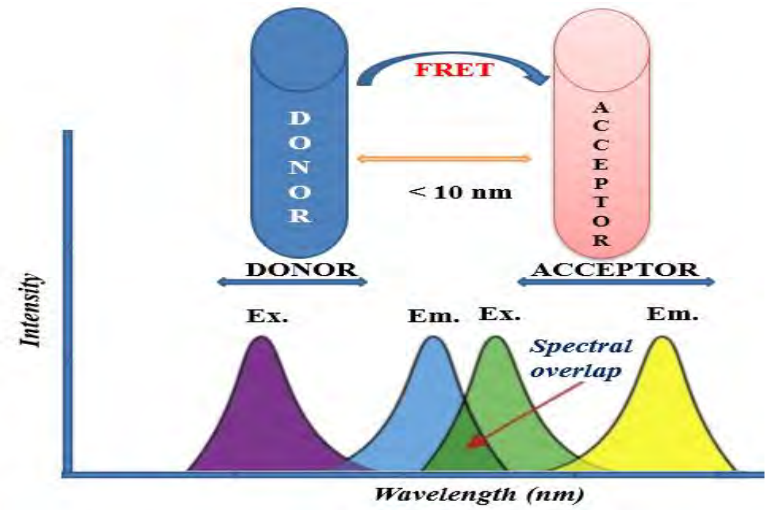

Figure-1.9. Schematic representation of the FRET process.

1.2.2.3.5. Excited-state intramolecular proton transfer (ESIPT)

ESIPT is a type of excited-state reaction that occurs in certain **D-A** systems. In ESIPT, the excited state of the "**D**" molecule undergoes a proton transfer to an adjacent "**A**" group, resulting in the development of a tautomer. During excitation, the structure and electrical dispersal of the chromophore alters when the protons shift from the basic to the acidic side. The chromophore first occurs in an enol state supported by an intramolecular H-bonding, as shown in **Figure-1.10**. This process can result in noteworthy alterations in the photophysical and chemical features of the system [41–43].

In EDA systems, ESIPT can occur when a "**D**" group and an "**A**" group are covalently linked in the same molecule. When the "**D**" group is excited, it can transfer a proton to the "**A**" group, leading to a new molecule with a different electronic structure. This process can result in a shift of the UV-visible and fluorescence spectra, and it can also lead to alterations in the chemical reactivity of the system. Moreover, ESIPT can be used to design new materials with unique photophysical and chemical features, such as fluorescent sensors and molecular switches. The ESIPT process can modulate the molecule's fluorescence features in these systems by altering the D-A system's protonation state. This can result in an alteration in the color under a 365 nm UV lamp or intensity, which can be used as a signal for detecting specific analytes or conditions.

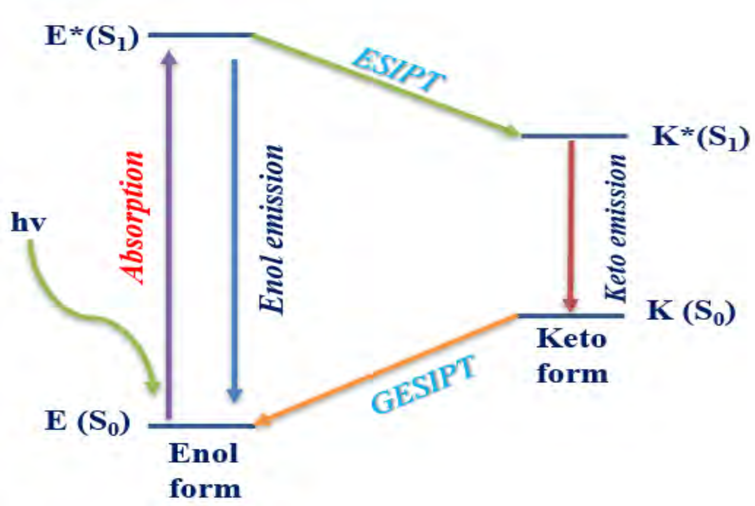

Figure-1.10. Mechanism of ESIPT process.

1.2.2.3.6. Excimer formation

Excimer formation is when two identical or similar chromophores, such as electron "**D**" and "**A**" molecules, interact to form an excited dimer or oligomer. In EDA systems, excimer formation can occur when the "**D**" and "**A**" molecules are in proximity, and their excited states interact through Coulombic and exchange interactions. The formation of an excimer in a **D-A** system can occur through several mechanisms, including ET, Et, and dipole-dipole interaction. In ET-based excimer formation, the excited "**D**" molecule transfers an electron to the "**A**" molecule, forming a charged species that can then interact through Coulombic interactions to form an excited state dimer. In Et-based excimer formation, the excited "**D**" unit transmissions its energy to the "**A**" unit, developing an excited state dimer through dipole-dipole interaction. The formation of an excimer in a **D-A** system can lead to alterations in the electronic and photophysical features of the system, including alterations in the UV-visible and fluorescence spectra, lifetime, and quantum yield. Excimer formation can also lead to alterations in the molecular packing and ordering of the system, as the formation of an excimer can affect the intermolecular interactions and packing in the system [44–46].

Excimer formation has been widely studied in various **D-A** systems, including organic semiconductors, fluorescent dyes, and biomolecules. Excimer formation is a significant process in the expansion of organic electronics and optoelectronic devices, as it can affect the performance and efficiency of these systems [47].

1.2.2.3.7. Aggregation-induced emission (AIE)

AIE is an intriguing occurrence observed in organic luminous substances derived from EDA systems. This unique phenomenon has significant applications in diverse fields, including organic light-emitting diodes for illuminating purposes and developing luminescent sensing materials like chemosensors and biosensors. Unlike solid states, most organic compounds' liquid states have higher fluorescence efficiencies. However, an ACQ effect frequently causes their fluorescence efficiency to be reduced in the aggregated state [47]. Their practical uses are constrained by this unique trait [48]. Fluorophores are covalently modified with bulky substituents and branched chains to prevent the ACQ effect, [49,50] and chromophores are shielded by cyclical molecular wires cheers to host-guest interactions [51,52]. Due to unrestricted intramolecular movements, certain organic molecules display poor emissive behavior in the liquid state. However, these exhibit significant fluorescence efficiency when aggregating in the solid form, a phenomenon known as AIE (see **Figure-1.11**). AIEE, another similar phenomenon, involves luminophores that display increased fluorescence in their solid state instead of their liquid state. Through electrostatic, coordination, hydrophobic, polar, and viscous interactions, analytes can alter how AIE molecules aggregate. As a result, several AIE-fluorescent sensors for recognizing ionic species, gases, and biomolecules have been created [53].

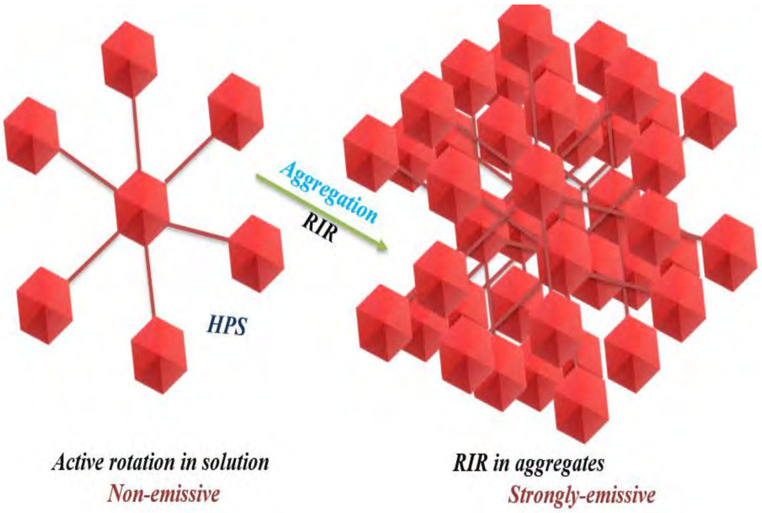

Figure-1.11. Pictorial representations of AIE.

1.2.2.4. Mode of operations of different chemosensors

1.2.2.4.1. Mode of operations of cation chemosensors

Cations are critical in various biological processes, including cellular regulation, muscle contraction activation, and nerve impulse transmission. They also serve as essential components in the active sites of enzymes, carrying out catalytic functions within biological systems. However, the introductory section states that deviations in cation levels, either in deficiency or excess, have been linked to specific diseases. Consequently, there is a need to develop cation sensors. The design of cation sensors revolves around non-covalent interactions between the binding site and the cation. Typically, constructing cation sensors involves combining an ionophore with a chromophore or luminophore to facilitate the selective detection of the target cation through changes in photophysical properties. These alterations arise from photoinduced processes such as ET, Et, and excimer/exciplex formation. The effectiveness and specificity of cation binding in the sensor depend on several factors, including the ligand topology, physical characteristics of the cation (such as coordination number, ionic radius, charge, and hardness), and the nature of the solvent (pH, polarity, ionic strength). Cation chemosensors, such as PET, ICT, and FRET, can be categorized based on the nature of their photoinduced interactions.

In an EDA-based system, a cation chemosensor works by binding to a specific cation through electrostatic or other interactions, leading to alterations in the electronic and photophysical features of the system. The mode of operation of a cation chemosensor in an EDA-based system can be described as follows:

(a) **Binding of the cation**: The cation chemosensor is designed to selectively bind to a specific cation through complementary electrostatic or other interactions, such as coordination or H-bonding. Upon binding to the cation, the electronic and photophysical features of the **D-A**-based system can be altered.

(b) **Alterations in the electronic structure**: The cation binding to the chemosensor can induce alterations in the electronic arrangement of the "**D**" and "**A**" moieties, leading to alterations in the UV-visible and fluorescence features of the system. These alterations can be used to detect the presence of the cation in the system.

(c) **Alterations in the photophysical features**: The binding of the cation to the chemosensor can also lead to alterations in the photophysical features of the system, such as alterations in the fluorescence wavelength, intensity, or lifetime. These alterations can be detected through fluorescence spectroscopy, time-resolved fluorescence, or other techniques.

The sensitivity and selectivity of a cation chemosensor in an EDA-based system can be improved by optimizing the design and structure of the chemosensor, including the choice of "**D**" and "**A**" moieties, the type and location of binding sites for the cation, and the use of appropriate linkers and spacers to control the distance and orientation between the "**D**" and "**A**" moieties [54–57].

1.2.2.4.2. Mode of operations of anion chemosensors

Anions play crucial roles in numerous biological and industrial processes. Moreover, their presence in the environment is essential for sustaining growth, but they can also act as harmful pollutants, necessitating their detection with significant attention. Over the past few years, the development of anion sensors has garnered considerable interest due to their fundamental involvement in environmental, chemical, and industrial processes. A promising and well-structured strategy for designing anion sensors involves the combination of a binding site with a signaling subunit. The binding site can consist of an organic compound such as EDA molecules or a metal-organic framework. At the same time, the signaling subunit changes spectroscopic properties, such as color or fluorescence, upon interacting with the anion [58–60]. However, developing selective anion chemosensors requires careful consideration of the following factors: (i) Ionic size: Anions typically have larger sizes than cations, necessitating receptors with dimensions larger than those designed for cations. (ii) Shapes: Anions display a wide range of geometrical shapes, including linear shapes (e.g., SCN^-, N_3^-), planar shapes (e.g., $PtCl_4^{2-}$, NO_3^-), spherical shapes (e.g., halides), tetrahedral shapes (e.g., PO_4^{3-}, SO_4^{2-}), octahedral shapes (e.g., PF_6^-), and even more complex shapes. (iii) Anions usually exhibit coordination saturation and tend to bind through weak van der Waals forces and hydrogen bonding, and (iv) Many anions are sensitive to changes in pH and exist only within a narrow pH range compared to cations.

However, anion sensors based on EDA systems are designed to selectively detect and quantify the existence of specific anions, such as halides or oxyanions, in a solution. The mode of operation of an anion sensor based on EDA systems typically involves the following steps:

(a) **Binding of the anion**: The anion chemosensor is introduced into a solution containing the target anion. The anion binds to the chemosensor molecule, instigating an alteration in the electronic and photophysical features of the molecule.

(b) **Alteration in photophysical features**: Upon binding the anion, the electronic interactions between the **"D"** and **"A"** moieties are altered, subsequently in the photophysical features of the molecule, such as an alteration in the fluorescence intensity or wavelength.

(c) **Detection and quantification**: The alteration in the photophysical features of the chemosensor molecule can be detected and quantified using several methods, including fluorimetric, spectrophotometric, and electrochemical techniques. The intensity or wavelength of the emitted illumination can govern the anion concentration in the solution.

Anion chemosensors developed from EDA systems have found various applications in sensing, imaging, and diagnostic applications. These chemosensors can be designed to sense a wide variety of anions, including halides and oxyanions, and can be tailored to have high selectivity and sensitivity for specific anions [61–66]. Moreover, there are three different approaches have been employed in the design of anion chemosensors, which is discussed in detail below:

1.2.2.4.2.1. Binding site-signaling subunit (BSSS) method

The BSSS method is a popular strategy for designing anion chemosensors in EDA systems. This method involves incorporating an anion-binding site within a larger EDA system, which can signal the presence of the bound anion through alterations in the photophysical features of the molecule. This method is often used for designing colorimetric and fluorescent anion chemosensors. Using fluorescent chemosensors as an example, **Figure-1.12** demonstrated the covalent introduction of binding sites and signaling subunits to the chemosensors [67]. In this method, the anion-binding site is typically a functional group or moiety capable of specifically interacting with the target anion. For example, halide anions can be selectively bind using H-bonding moieties such as ureas or thioureas, while other anions, such as phosphate, can be bind through metal coordination [68–71]. The EDA system is designed to have a "**D**" and "**A**" moiety connected through a conjugated linker. When the anion binds to the anion-binding site, the EDA interaction is altered, leading to an alteration in the photophysical features of the molecule.

The BSSS method can be used to design anion chemosensors for diverse applications, including sensing, imaging, and diagnostic applications. The advantages of this method include its high selectivity and sensitivity and the ability to tailor the anion-binding site to specific anions of interest. Additionally, the EDA system can have a range of photophysical features, allowing for the development of chemosensors with various detection methods.

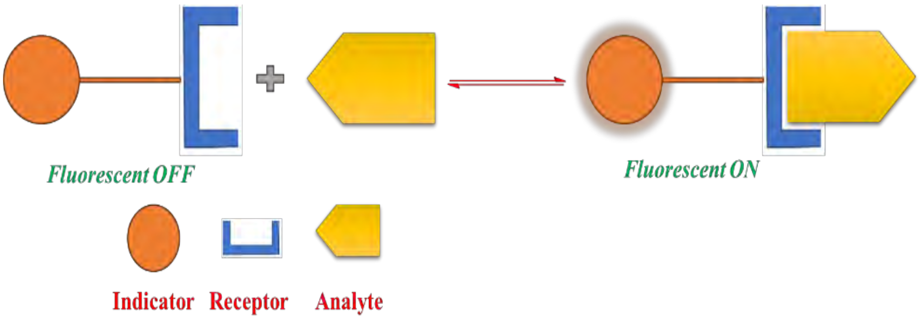

Figure-1.12. Schematic representation of the BSSS approach.

1.2.2.4.2.2. Displacement Approach

The displacement approach is a strategy for designing chemosensors for EDA systems that detect specific analytes, such as ions, molecules, or biomolecules. In the displacement approach, a pre-existing host-guest complex is modified by introducing a competitive guest that can selectively displace the original guest from the host cavity. The displacement of the original guest can be monitored through alterations in the photophysical features of the EDA system.

In an EDA system, the host is usually an electron-rich molecule, which can form a stable complex with an electron-deficient guest molecule. The original guest molecule may have weak binding affinity or selectivity for the host. To improve the selectivity and sensitivity of the system towards a specific analyte, a competitive guest molecule is introduced, which has an enhanced binding affinity or selectivity for the host than the original guest. Taking fluorescent chemosensors as an example, **Figure-1.13** demonstrates how a coordination complex (displacement approach), in which the presence of anions, revives the noncoordinated spectroscopic behavior of indicator [67].

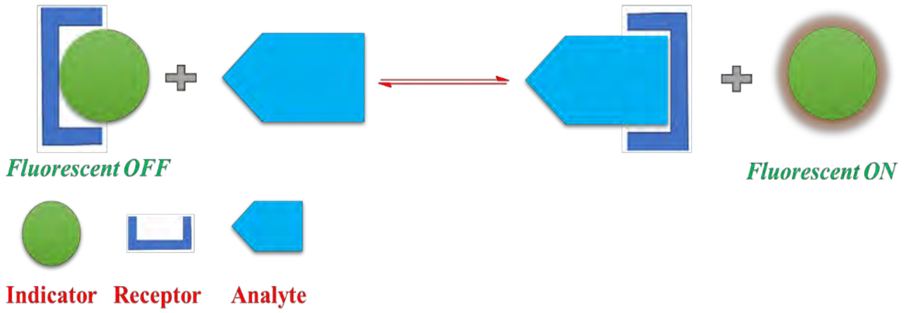

Figure-1.13. The displacement strategy is depicted schematically.

1.2.2.4.2.3. Chemodosimeter Approach

In the chemodosimeter approach, a specific analyte is detected through a chemical reaction, typically an irreversible process, which leads to discernible alterations in the optical signal. As depicted in **Figure-1.14**, when a target anion undergoes a reaction with the chemodosimeter, it can either form a covalent bond with the chemodosimeter or catalyze a chemical reaction. Consequently, in both scenarios, a novel product distinct from the initial constituents is generated, resulting in changes in the optical properties of the solution. This characteristic enables the identification and quantification of the anion under investigation.

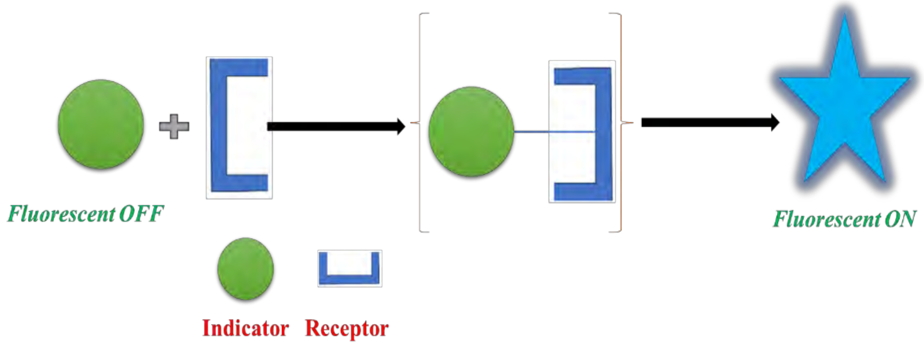

Figure-1.14. The chemodosimeter approach is depicted schematically.

1.2.2.5. Mode of action of pH chemosensors

The mechanism of acid-base detection by an EDA-based chemosensor involves an alteration in the sensor's optical, electrical, or magnetic features in response to alterations in the analyte's concentration or pH. One common mechanism of acid-base detection by chemosensors is using pH-sensitive dyes, which alter color in response to changes in pH. These dyes are often attached to a polymer or other support material immobilized in a solid matrix, or coated onto a surface. When an acid or base interacts with the sensor, the pH-sensitive dye changes color and this alteration can be detected by various methods, such as fluorescence, absorbance, or reflectance [72–75].

Another mechanism of acid-base detection by chemosensors is based on the practice of ion-selective membranes or electrodes. These sensors work by measuring the activity or concentration of specific ions in a solution, which are related to the pH of the solution. The membrane or electrode is typically made of a selective ionophore that selectively binds to a specific ion, such as H^+ or OH^-, and generates an electrical signal proportional to the concentration of that ion in the solution. The mechanism of acid-base detection by an EDA-based chemosensor depends on the sensor's specific design and the detected analyte's features. However, all chemosensors rely on a specific recognition mechanism to selectively interact with the analyte of interest and generate a confined response.

1.2.2.6. Mode of action of nitroaromatic compounds (NACs) chemosensors

In the case of nitroaromatic detection, EDA-based chemosensors are designed to recognize and interact with the nitro group ($-NO_2$) present in NACs. The mechanism of NAC detection by a chemosensor typically involves a recognition event and a transduction event. During the recognition event, the chemosensor recognizes and binds selectively to the nitro group of the NAC. Numerous processes might lead to this identification, including H-bonds, electrostatic interactions, and π-π-interactions. Once the recognition event has occurred, a transduction event is triggered, resulting in a confined alteration in the physical or chemical features of the chemosensor. This alteration can be identified using various methods, such as fluorescence, colorimetry, electrochemistry, or SERS. For example, in the case of a fluorescent chemosensor, the binding of the NAC to the chemosensor causes an alteration in the fluorescence intensity or wavelength, which can be measured using a fluorescence spectrophotometer. Similarly, in the case of a colorimetric chemosensor, the binding of the NAC to the chemosensor causes an alteration in the color of the solution, which can be sensed using the bare eye or a colorimeter [76–80].

1.2.2.7. Mode of action of nerve agent chemosensors

In recent decades, the significance of developing colorimetric and fluorescence-based chemosensors for detecting chemical warfare agents (CWAs) has steadily increased. Presently, two primary detection approaches are employed: (i) reaction-based or activity-based sensing and (ii) receptor-based sensing. The reaction-based approach utilizes the reactivity between the analyte and a functional group present in the chemical sensor. This interaction results in a measurable optical response. However, this strategy is generally irreversible, meaning the sensor cannot be reused for subsequent detection.

Conversely, using a supramolecular approach, CWAs can be detected through non-covalent, reversible interactions. This approach allows for the possibility of reusing chemical sensors. However, the supramolecular method often lacks selectivity and sensitivity, leading to frequent false positive responses. Detecting nerve agents involves exploiting the reactions between nucleophilic functionalities on a probe and electrophilic phosphate esters. This chemical reaction produces a detectable optical signal, which can be colorimetric and/or fluorescence changes. These changes can be achieved by suppressing PET, and ICT, or by triggering an intramolecular cyclization reaction (as depicted in **Figure-I.15**). A more recent strategy involves detecting hydrolyzed products resulting from the decomposition of nerve agents [81]. These hydrolyzed products include fluoride ions, CN ions, and thiols (as shown in **Figure-I.15e**).

Numerous research groups worldwide are continuously dedicating significant efforts to devise new and alternative strategies for designing and developing advanced chemical sensors for CWAs detection [82–84].

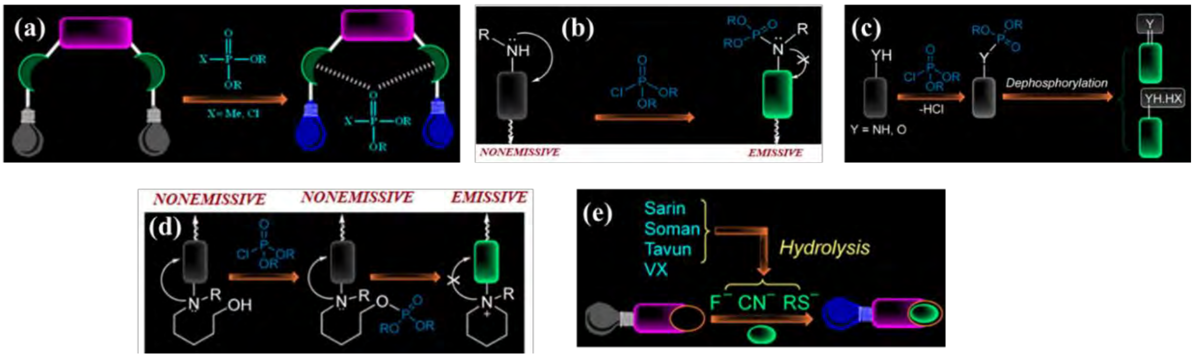

Figure-1.15. Illustrates the fundamental schematics detailing diverse detection mechanisms employed for nerve agents. **(a)** indicator-spacer-receptor configuration, **(b)** amino phosphorylation of sensors, **(c)** phosphorylation and dephosphorylation dynamics, **(d)** intramolecular cyclization upon hydroxyl phosphorylation, and **(e)** optical detection of hydrolyzed nerve agent products, namely F^{-}, CN^{-}, and thiols.

1.3. Aim and objectives of the present thesis work

In conclusion, EDA systems are an important class of materials with unique photophysical features. These systems consist of two or more components where one turns as an electron “**D**” and the other as an electron “**A**”. EDA systems' photophysical behavior is related to how they absorb, emit, and transfer energy. They typically have strong UV-visibility in the visible and/or near-infrared region, which can be tuned by changing the identity and arrangement of the “**D**” and “**A**” units. Upon excitation, the excited state energy can be transferred from the “**D**” to the “**A**”, resulting in fluorescence from the “**A**” or dissipative decay. The efficiency of electron transfer in EDA systems depends on several factors, such as the energy level alignment between the “**D**” and “**A**”, the distance between them, and the overlap between the “**D**” fluorescence and “**A**” absorption spectra. Controlling these factors makes it possible to design EDA systems with high ET efficiency and unique photophysical features, such as enhanced fluorescence and phosphorescence. EDA systems offer a promising approach to developing new materials with advanced functionality and performance, including organic photovoltaics, light-emitting diodes, sensors, and bioimaging.

The aim of the present thesis work is to investigate the photophysical and sensorial behavior of various chromophoric systems comprising EDA units. This research work pursues to widely recognize the interactions within these molecular structures and their impact on both photophysical properties, such as absorption and emission spectra, and sensorial characteristics, including color perception and responsiveness to external stimuli such as acid-base, anions, metal cations, NACs, and CWAs. The objectives include synthesizing different chromophoric systems, characterizing their electronic structures, exploring their photophysical properties through spectroscopic techniques, and assessing their sensorial attributes. The findings aim to contribute valuable insights to the field of molecular design for applications in areas such as optoelectronics and sensory materials.

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