INTRODUCTION

1. INTRODUCTION:

In the context of chemistry, a sensor is a device or molecule that detects and responds to specific chemical species or reactions. This detection often produces a measurable signal or change in color, fluorescence, or electrical properties [1]. Chemical sensors can be designed to detect a wide range of analytes, including ions, molecules, and biomolecules. They have various applications, such as environmental monitoring, medical diagnostics, and industrial process control. There are different types of chemical sensors, including electrochemical, optical, and biochemical sensors, each with its own sensing mechanism and advantages. Chemical sensors play a crucial role in understanding chemical systems, monitoring chemical reactions, and detecting chemical contaminants [1]. Their development and application continue to evolve with advances in materials science, nanotechnology, and analytical chemistry. This enables researchers to create new sensors with improved sensitivity, selectivity, and detection limits, expanding their potential applications in various fields [1,2].

Chemical sensors are also used in environmental monitoring, detecting pollutants in air and water. They help track climate change by monitoring greenhouse gases and ozone layer depletion. In the medical field, chemical sensors detect biomarkers for diseases like diabetes, cancer, and Alzheimer's. They also monitor drug levels and toxicity [1-3]. Industrial processes rely on chemical sensors to control emissions, monitor chemical reactions, and optimize production. They ensure safety and efficiency in various industries, from petrochemicals to food processing. Chemical sensors are also used in security and defense, detecting chemical weapons and explosives [4]. They help protect people and environments from harmful substances. Advances in chemical sensors have led to miniaturization, enabling portable and wearable devices. This has opened up new possibilities for point-of-care diagnostics, personal health monitoring, and environmental monitoring [5,6].

The future of chemical sensors holds much promise, with emerging technologies like nanotechnology, graphene, and artificial intelligence. These innovations will further enhance sensitivity, selectivity, and detection limits, leading to even more exciting applications [2-7]. As research continues to push boundaries, chemical sensors will play an increasingly vital role in improving our lives, environments, and understanding of the world around us.

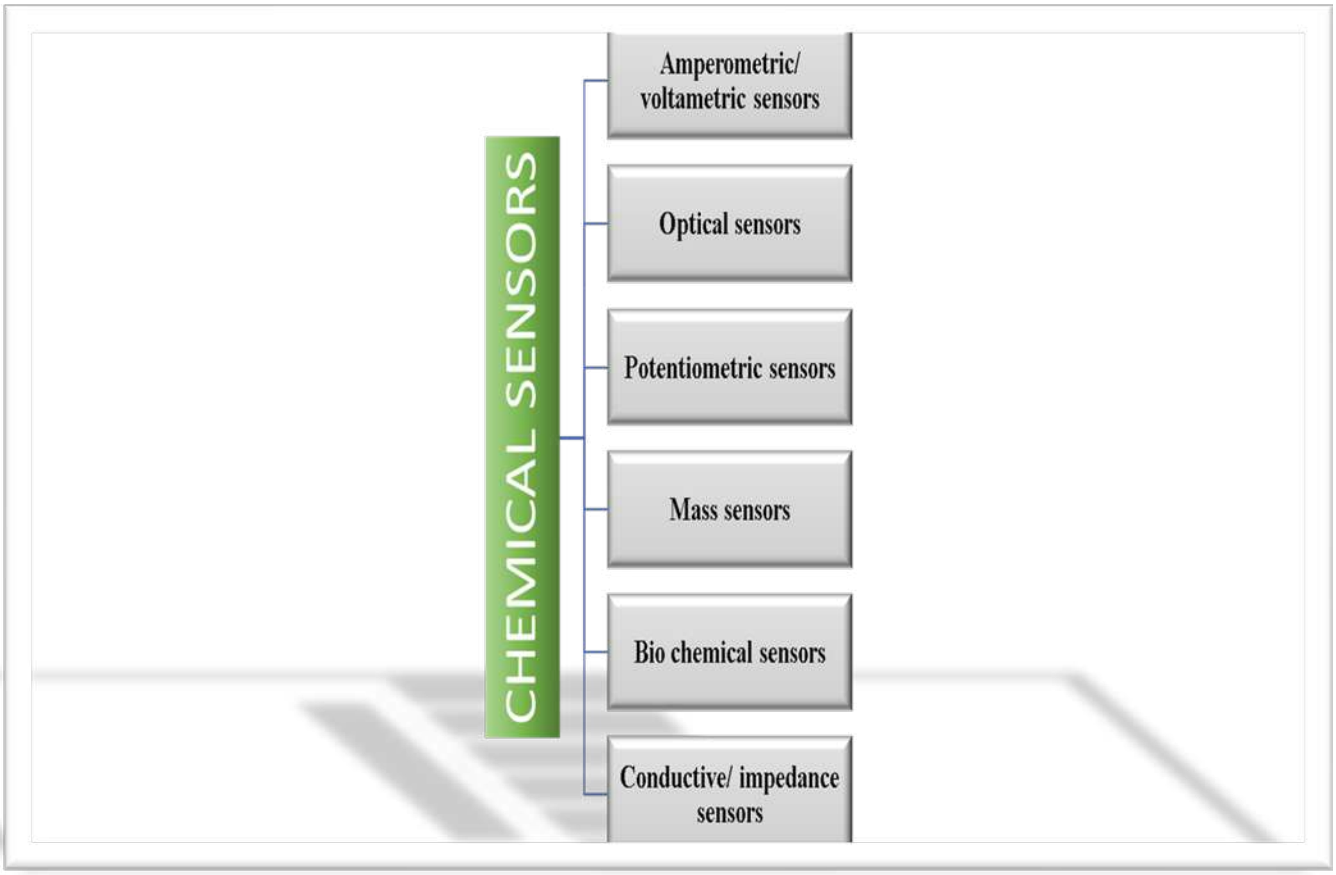


Figure 1. Types of chemical sensors

1.2.1 COMPONENTS OF CHEMICAL SENSOR:

All chemical sensors have two components.

Receptor:

The receptor is the sensing element that interacts with the chemical species being detected. Its purpose is to recognize and bind the target molecule, triggering a response [5-10]. Receptors can be:

- Biological molecules: Enzymes, antibodies, DNA, or proteins that bind specifically to the target molecule.
- Chemical molecules: Synthetic molecules designed to interact with the target molecule.
- Metal oxides: Materials like SnO_2 or ZnO that respond to changes in chemical composition.

- The receptor's binding properties and selectivity determine the sensor's sensitivity and specificity.

Transducer:

The transducer converts the chemical information from the receptor into a measurable signal. It amplifies and processes the signal, making it suitable for output [5-10]. Transducers can be:

- Electrochemical: Measure changes in current or potential due to the chemical reaction.
- Optical: Detect changes in light absorption, fluorescence, or refractive index.
- Thermal: Measure heat generated by the chemical reaction.
- Piezoelectric: Detect changes in mechanical properties, like vibration or pressure[10].

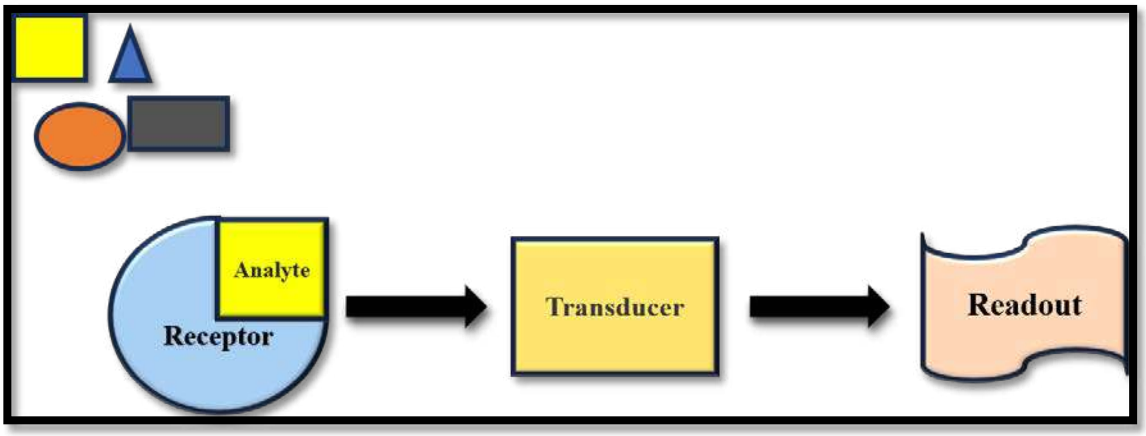


Figure 2. General representation of working principle of sensor.

1.2. OPTICAL SENSOR:

Optical sensors play a vital role in chemistry, enabling the detection and analysis of various chemical species and reactions. These sensors utilize light to interact with molecules, allowing for the measurement of chemical properties and concentrations. In chemical sensing, optical sensors detect changes in light absorption, fluorescence, or phosphorescence, which are correlated to the presence and amount of specific chemicals. This enables the monitoring of chemical reactions, detection of contaminants, and analysis of sample composition [3-5].

Optical sensors are particularly useful in chemistry due to their high sensitivity, selectivity, and non-invasive nature. They can detect trace amounts of chemicals, making them ideal for applications such as environmental monitoring, food safety, and pharmaceutical analysis [10]. Additionally, optical sensors can be designed to target specific chemical species, allowing for precise detection and quantification. In chemical synthesis, optical sensors enable real-time monitoring of reactions, optimizing conditions and yields. Overall, optical sensors have revolutionized the field of chemistry, providing a powerful tool for chemical analysis and detection. Optical sensors have also enabled the development of novel analytical techniques, such as surface-enhanced Raman spectroscopy (SERS) and surface plasmon resonance (SPR), which offer enhanced sensitivity and selectivity for chemical detection [6]. SERS uses nanoparticles to amplify Raman signals, while SPR utilizes gold or silver surfaces to detect changes in refractive index. These techniques have enabled the detection of chemicals at the single-molecule level, allowing for early detection of diseases, monitoring of environmental pollutants, and quality control in industrial processes [10].

Furthermore, optical sensors have facilitated the integration of chemistry with other disciplines, such as physics and engineering, leading to innovative applications in areas like optofluidics and lab-on-a-chip devices. Optofluidics enables the manipulation of fluids and chemicals using light, while lab-on-a-chip devices integrate multiple analytical techniques on a single platform. The versatility of optical sensors has also led to their use in security and defense applications, such as detecting chemical and biological agents [9,10].

Additionally, optical sensors have enabled the development of novel materials and surfaces, such as metamaterials and nanostructured surfaces, which offer enhanced optical properties and sensing capabilities. Metamaterials can be designed to have specific optical properties, while nanostructured surfaces can enhance light-matter interactions. These materials and surfaces have enabled the development of novel optical sensors with enhanced sensitivity and selectivity [5].

Overall, optical sensors have revolutionized the field of chemistry, enabling novel analytical techniques, materials, and applications. As research continues to advance, optical sensors are expected to play an increasingly vital role in shaping the future of chemistry and interdisciplinary research [2-9].

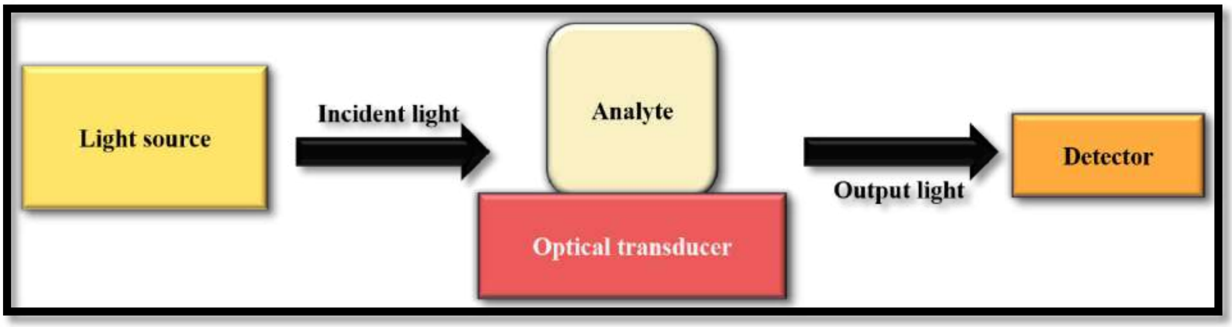


Figure 3. Schematic diagram for optical sensor.

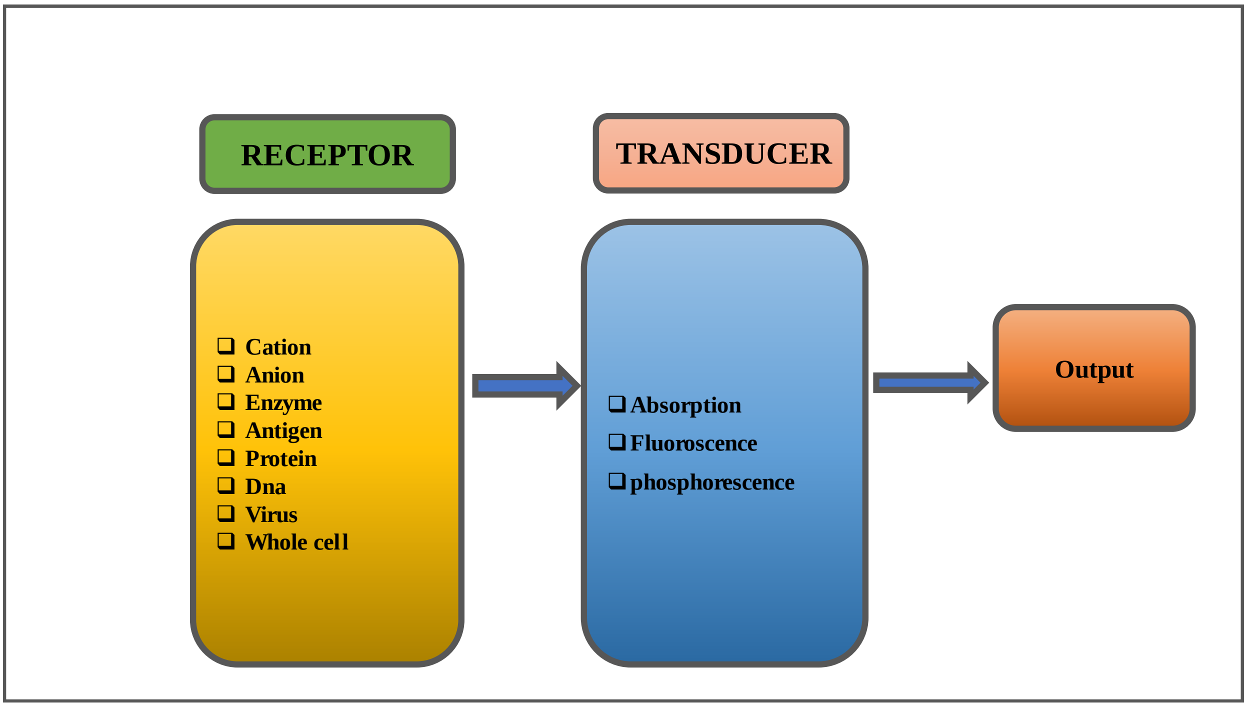


Figure 4. General classification of optical based sensor

Figure 5. Optical sensors in chemistry utilize various techniques

Chemical optical sensors detect changes in light properties (e.g., intensity, wavelength, polarization) upon interaction with the analyte, enabling:

- Quantification of chemical species
- Monitoring of chemical reactions
- Detection of chemical contaminants
- Analysis of biological samples (e.g., DNA, proteins)

Examples of chemical optical sensors include:

- pH sensors (e.g., pH-sensitive dyes)
- Oxygen sensors (e.g., luminescent dyes)
- Glucose sensors (e.g., enzyme-based assays)

- Chemical warfare agent detectors (e.g., nerve gas sensors)
- Environmental monitoring sensors (e.g., water quality sensors) [5-9]

TYPES:

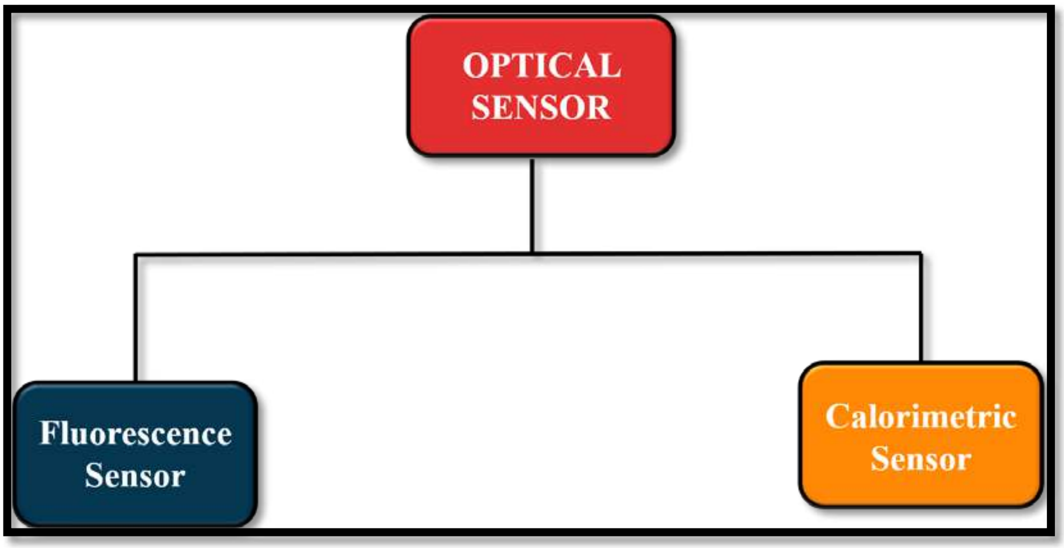


Figure 6. Types of optical sensors

1.2.1 CALORIMETRIC SENSOR

Colorimetric chemosensing technique is a promising technique allowing qualitative and quantitative detection of medically and environmentally important ionic or neutral species without any sophisticated instrumentation. Its utilization as a test kit for on-site detection, short-time detection, simplicity, reversibility alongwith high selectivity and sensitivity, which does not need any pre-treatment of sample and manual expertise, makes it a desirable technique among the researchers.The heat change is directly proportional to the amount of substance present or the rate of reaction, allowing the sensor to quantify the analyte[2]

The colorimetric determination of cations have been achieved utilizing various photoactive moieties such as pyrene, BODIPY, anthracene, rhodamine, fluorescein, nitrophenyls, julolidine, 1,8-naphthalimide, Near Infra Red (NIR) absorbing dyes (squarines, hemocyanines), coumarin, nitrobenzoxazole (NBD), etc. (several of which act as chelators as well) conjugated to an appropriate binding unit mainly through Schiff base, diazo and amide linkages. More precisely, the increased conjugation/electron density in the sensor molecule results in the red shift of the absorption band and decreased conjugation/electron density results in blue shift with relevant changes in the color enabling chromogenic detection

A calorimetric sensor is a device that measures the heat absorbed or released during a chemical reaction or physical process. It detects changes in temperature or heat flow, allowing for the quantification of thermodynamic parameters such as:

- Enthalpy (H)
- Entropy (S)
- Heat capacity (Cp)
- Heat of reaction (Q)

Calorimetric sensors are used to study various phenomena, including:

- Biomolecular interactions (e.g., protein-ligand binding)
- Enzyme kinetics and inhibition
- Protein folding and stability
- Nanomaterials' thermal properties
- Chemical reactions and catalysis
- Phase transitions and thermodynamic properties

Common types of calorimetric sensors include:

- Differential Scanning Calorimeters (DSC)
- Isothermal Titration Calorimeters (ITC)
- Heat Conduction Calorimeters
- Calvet-Type Calorimeters
- Microcalorimeters

These sensors offer high sensitivity, precision, and accuracy, making them a valuable tool in various fields, including biotechnology, pharmaceuticals, food safety, environmental monitoring, materials science, and nanotechnology[2,3].

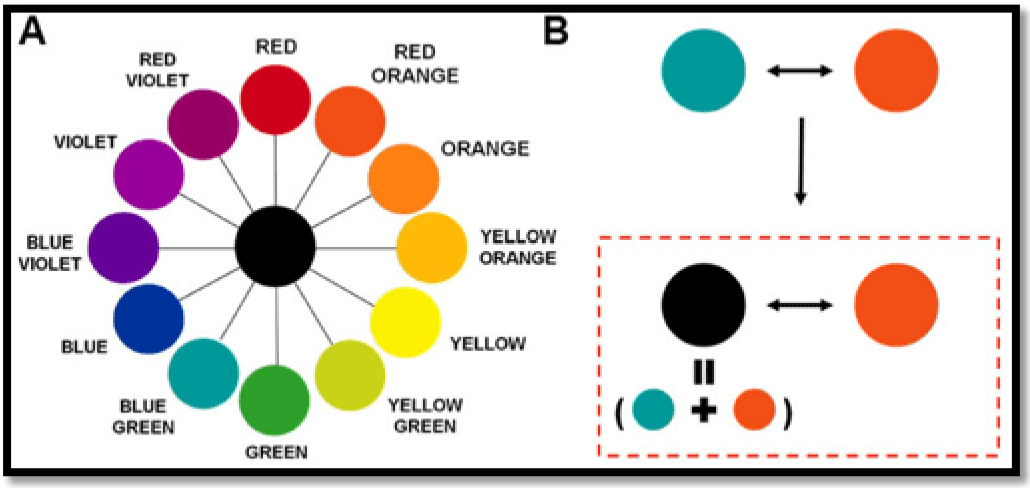


Figure. 7. Schematic Diagram of Calorimetric Color Change

1.2.2. FLUROSCENSE SENSOR:

A fluorescence sensor is a highly sensitive and selective analytical tool that detects and measures the fluorescence emission of a sample. It consists of a light source, a sample chamber, a detector, and associated electronics. The light source excites the sample, causing it to emit fluorescence, which is then detected by the detector. The detector converts the fluorescence signal into an electrical signal, which is amplified and processed by the electronics to produce a measurable output.

Fluorescence sensors operate on the principle of fluorescence spectroscopy, which is based on the phenomenon of fluorescence emission by molecules when excited by light. The sensor measures the intensity and wavelength of the fluorescence emission, which is directly proportional to the concentration of the analyte. The sensor can be designed to detect specific molecules or ions by tuning the excitation wavelength and detection wavelength to match the fluorescence characteristics of the target molecule [6-8].

There are various types of fluorescence sensors, including:

- Intensity-based sensors: Measure the intensity of fluorescence emission.
- Lifetime-based sensors: Measure the decay time of fluorescence emission.
- Polarization-based sensors: Measure the polarization state of fluorescence emission.
- Fiber-optic sensors: Use optical fibers to detect fluorescence emission.
- Nanoscale sensors: Use nanoparticles or nanostructures to enhance fluorescence detection.

Fluorescence sensors have revolutionized the field of analytical chemistry, enabling rapid, sensitive, and selective detection of molecules and ions. Their versatility and miniaturization capabilities make them an essential tool for various applications.A fluorescence sensor is a device that detects and measures the fluorescence emitted by a substance when excited by light. It consists of:

- Light source (e.g., LED, laser)
- Excitation filter (selects specific wavelength)
- Sample chamber (contains the substance)
- Emission filter (selects specific wavelength)
- Detector (e.g., photodiode, PMT)
- Signal processing unit

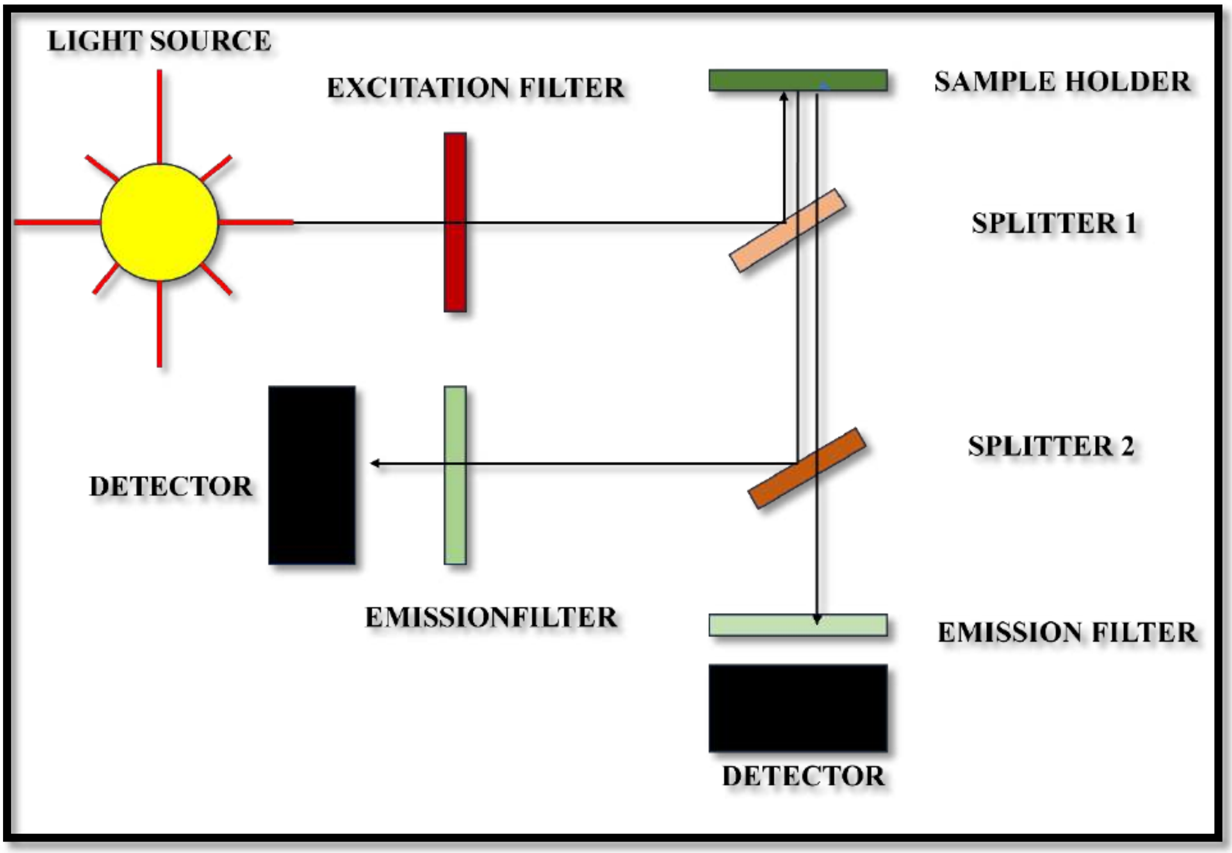


Figure 8. Schematic diagram of fluorimetric sensor

The sensor works by:

- Exciting the substance with light
- Measuring the emitted fluorescence
- Comparing the signal to a reference or calibration standard

Fluorescence sensors are used in:

- Biomedical research (e.g., protein analysis, cell imaging)
- Environmental monitoring (e.g., water quality, air pollution)
- Food safety testing (e.g., bacterial contamination)
- Chemical detection (e.g., heavy metals, pesticides)
- Medical diagnostics (e.g., cancer detection, glucose monitoring)

Advantages:

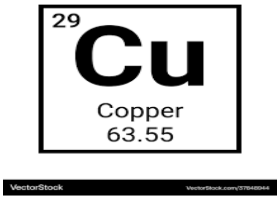
- High sensitivity and selectivity
- Real-time measurements
- Non-destructive testing
- Compact and portable designs

- Multiplexing capabilities (detecting multiple analytes simultaneously)

Fluorescence sensors play a vital role in various applications, enabling the detection and quantification of substances with high accuracy and speed [5-10].

1.3. COPPER:

Copper is an essential micronutrient for both animals and plants. It acts as a critical cofactor in various biological processes including hematopoiesis, collagen and enzymes synthesis. However, the excessive copper is toxic to living beings. In toxic concentrations, it leads to the increasing level of oxidative stress and disorders, and then causes some neurodegenerative diseases, such as Alzheimer's, Menkes and Wilson disease, as well as inhibits the plants' growth and mineral nutrient uptake. Besides, mercury is one of the most toxic heavy metals. It has bio-accumulation and high toxicity, which causes irreversible damages, such as neurological abnormalities, gingivitis, and tumor formation, even at a very low concentration. Therefore, it is essential to develop approaches for Cu(II) concentration monitor. Among numerous methods, fluorescence method has drawn tremendous attentions on account of its remarkable performance, such as high selectivity, good sensitivity, rapid response and easy operation.[11]



Cu(II) is an essential trace element for many biological processes and has been regarded as a significant environmental pollutant due to its widespread use. Since excessive Cu(II) intake can cause serious human diseases, the detection and quantification of Cu(II) in environmental and biological monitoring are thus of importance. Recently, there have been increasing number of reports on alternative methods using colorimetric sensors and fluorescence sensors, with varying degrees of success regarding sensitivity, selectivity and stability.[12]

Copper works in combination with certain proteins to produce enzymes as catalysts to assist many body functions [13]. Research suggests that copper misregulation is one of the factors leading to an increased risk of developing coronary heart disease [14]. Also, misregulation of copper is a cause of many human genetic and metabolic disorders [15]. Recently, copper has also been discovered to regulate cancers operating through widely observed oncogenic BRAF mutations [16]. It also helps in the melanin transformation for pigmentation of the skin and also to cross-link collagen and elastin for the maintenance of connective tissues [17]. The biochemistry of copper ion (Cu^{2+}) in eukaryotic cells is diverse, it serves as an important cofactor for several redox enzymes which react with dioxygen and its derivatives like superoxide. These enzymes also participate in body processes such as pigmentation (tyrosinase), epigenetic modification (lysyl oxidase-like 2), respiration (cytochrome *c* oxidase), iron uptake (ceruloplasmin), defense by antioxidants (Cu/Zn superoxide dismutase), synthesis and metabolism of neurotransmitter (dopamine *β*-hydroxylase), and dietary amines handling (Cu^{2+} amine oxidases) [18]. The human body can be exposed to Cu^{2+} through contaminated water by industrial or consumer waste or by heavy metals from soil occurring due to acid rain. On considering these impacts, the Environmental Protection Agency recognizes Cu^{2+} as a potential trace pollutant so sets a permissible amount in drinking water as 1.3 ppm or 20 μM of Cu^{2+} [19]. In humans, the average concentration of Cu^{2+} in blood is 100–150 μg dL^{-1} (15.7–23.6 μM) [20]. Therefore, the monitoring of Cu^{2+} both in drinking water and in different environmental sources is necessary.

1.3.1. COPPER SENSOR:

Several methods for the determination of copper ions at the trace quantity level have been proposed. They include atomic absorption spectroscopy (AAS) [21], inductively coupled plasma atomic emission (ICP-AES) [22], inductively coupled plasma mass spectroscopy [23], spectrophotometry [24], and anodic stripping voltammetry [25]. These methods need relatively high-cost apparatus and are not easily adaptable for online monitoring. Therefore, a growing interest has evolved in different laboratories for the development of metal ion monitoring chemical sensors. Chemical sensors based on optical signal measurements have been accepted as advantageous because they can be miniaturized and can be manufactured at low cost [26], [27]. Optical sensors are capable of continuously record a chemical species and thus have found numerous applications in areas such as the chemical industry, in biotechnology and medicine [28].

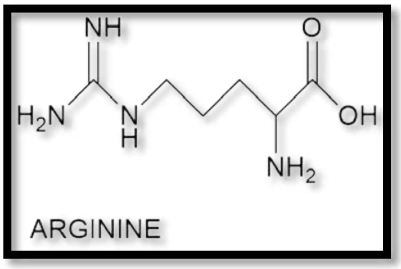
Recent years have seen a large number of publications dealing with optical Cu^{2+} sensing. Most of these are based on either absorbance [29], [30] or reflectance [31] measurements of immobilized colorimetric reagents in various matrices. Although fluorescence is advantageous over absorbance and reflectance in terms of sensitivity, only a few optical sensors based on fluorescence are reported for Cu^{2+} determination. Fluorescent sensors for Cu^{2+} based on calcein [32] or rhodamine derivatives [33] as fluorophores have been published. Unfortunately, these sensors suffer from being relatively unspecific and, therefore, many ligands have been synthesized and examined for preparation of Cu^{2+} sensing membranes [34], [35].

1.4. AGGREGATION INDUCED EMISSION (AIE):

Aggregation-induced emission luminogens (AIEgens) have emerged as a novel type of advanced material with excellent performance in various fields. Much effort has been devoted to determining the AIE mechanism(s) by theoreticians and experimentalists. Restriction of intramolecular motion has been recognized as the general working mechanism of AIE. AIE research has now gained extensive attention and AIEgens have been recognized as an important type of advanced functional material for a wide variety of applications [36]. Deciphering its working mechanism is not only of fundamental importance but also beneficial for providing design guidelines for the development of new AIE systems for new practical applications. Although some debate still exists, restriction of intramolecular motions (RIM) has been generally accepted as central to the AIE working mechanism. According to the RIM mechanism, it can be concluded that structural rigidification in high viscosity media, low temperature, and doping of chromophores in rigid matrices can also lead to strong emission. Thus aggression is not necessary for strong emission on some occasions. As AIEgens often show unique advantages such as high solid quantum yield, high photostability and no ACQ (Aggregation caused quenching) effect, they have been successfully applied in various fields such as OLEDs, stimuli responsive sensing, bioimaging and theranostics [32-36]. In this brief focus article, an overview of the current fundamental understanding of the AIE working mechanism, clarification of the existing controversies and disputes, and discussion of the future developments in AIE research are provided. To investigate the AIE working mechanism, first the structural difference between typical AIEgens and ACQ dyes should be understood. Distinctly different from the large planar structures of conventional ACQ dyes, most of the AIEgens show highly twisted propeller-like structures. This suggests that the twisted structure plays a critical role for the AIE phenomenon. It is reasonable to postulate that the intramolecular motions (rotation and vibration) of the AIEgens such as tetraphenylethene (TPE) and silole are rapid in dilute solution and the emission is quenched because of the high nonradiative decay rate (knr). However, because of the highly twisted conformation of AIEgens, both intermolecular p–p stacking and intramolecular motions are restricted in the aggregate or solid state which results in a suppressed k [36].

1.5. DUAL SENSOR:

Nowadays, amino acids play an important role in several key functions of cell regulation and metabolism in the human body [37,38]. Among multitudinous amino acids, arginine (Arg) is the most advantageous natural amino acid [39], and exhibits the most unique property of high basicity in the natural amino acids due to the unique guanidine unit [40]. Although it is regarded as a semi-essential or conditionally essential amino acid, it plays a key role in the normal operation of biological systems, such as cell division, wounds healing, converting ammonia into innocuous urea, especially in the regulation of gene, glycoprotein targeting, and vesicle transport [41-44]. Nevertheless, superfluous Arg in the body may cause anaphylactic reactions and increase stomach acid contents [45]. On the other hand, the deficit of Arg is also harmful to human health, such as retarded growth, hair decoloration, liver and skin damage, and so on [46]. Therefore, it is very important to detect the levels of Arg in environment and biology.



Recently years, with the rapid development of economy, the application of copper in mining, smelting, and industrial and agricultural wastes fields has resulted in increasing levels of Cu^{2+} in the environment and accumulation of Cu^{2+} in the food chain [47,48], leading to destruction of the environment and human health. Therefore, real-time monitoring of Cu^{2+} levels in the environment is very important. Up to now, various analytical techniques have been developed for the detection of Cu^{2+} or Arg, such as high-performance liquid chromatography [49,50], mass spectrometry of liquid chromatography–tandem [51], electrochemical method [52,53], colorimetric/fluorescent sensor [54], and so on. Among these methods, colorimetric/fluorescent sensors are considered as one of the most promising approaches in virtue of the merit of simplicity, high sensitivity, fast response and real time analysis [55,56]. Because the others methods need large instruments and equipment, the pretreatment of samples is complex, time-consuming, and could not be detected in real time. Although there are widespread reports on the colorimetric sensors of Cu^{2+} [57-63] and fluorescent-colorimetric sensors of Arg [64-66], the sensors for simultaneous detecting Arg and Cu^{2+} have rarely been reported [67,68]. Therefore, it is necessary to design novel sensors to meet the demands of the development of human society.

Table 1: Reported molecule for dual sensors (metal and amino acids)

S.No	**Molecule**	**Technique**	**Sensor**	**LOD (nm)**	**Ref**
1	I°	Calorimetry	Arginine & Cu^{2+}	0.9 & 0.3	[69]
2	PAR	Calorimetry	Cystine & Cu^{2+}	0.7 & 0.3	[70]
3	AIP	Fluorimetry	Cystine, Cu^{2+} & Fe^{3+}	200, 87.3 & 30.1	[71]
4	PQD	Fluorimetry	Creatinine & Cu^{2+}	-	[72]
5	IPY	Fluorimetry	Arginine, & Lysine	5.2 & 14.6	[73]
6	CAS	Calorimetry	Cu^{2+}, Ag^{+}, Fe^{3+} & Tryptophan	214, 99, 140 & 60000	[74]
7	WBCUS	Fluorimetry	Cysteine & Ag^{+}	1.0 & 5.0	[75]
8	Cdte@ZIF-365	Ratiometry	Histidine & Cu^{2+}	50 & 560	[76]
9	AUNCS	Calorimetry	Histidine & Cu^{2+}	20 & 0.1	[77]
10	Intrinsic dual-emitting CdS-Cu^{2+}	Ratiometry	Aspartic acid & Cu^{2+}	120 & 7.0	[78]
11	Cu-Cd	Ratiometry	Tryptophan & Fe^{2+}	275 & 46	[79]
12	Calix[4]arene	Calorimetry	Tyrosine & Cu^{2+}	1200 & 2.0	[80]

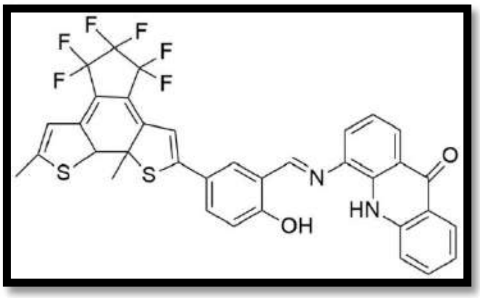


Figure 9. I°

A novel multi-functional sensor I° for Arg and Cu^{2+} was designed and synthesized successfully. The sensor could be used for the detection of Arg through fluorescent and colorimetric methods, and for the recognition of Cu^{2+} by colorimetric method with high selectivity and sensitivity. The sensor not only could achieve good recovery of Arg in simulated urine test, but also could be made into test strips for the recognition of Cu^{2+} with naked eyes. Moreover, it could be applied into the determination of Cu^{2+} in practical samples of water with satisfactory recoveries. Based on these results, the study may be applied into the biologic fluorescence labeling and the detection of practical water samples, and would provide some innovative strategies for the design and preparation of multi-functional sensors for biochemical and environment analysis [69].

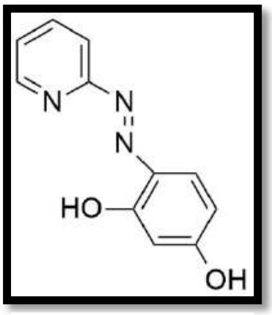


Figure 1O. PAR

An IDAs based chemosensing ensembles for sensitive and selective sequential detection of Cu^{2+} and cysteine (Cys) in 100% aqueous solution was designed on the basis of the complex formation between 4-(2-Pyridylazo) resorcinol (PAR). PAR was used for colorimetric detection of Cu^{2+} in aqueous solution by the obvious color change. The detection limit (31.0 nmol L^{-1}) for Cu^{2+} much lower than the guideline (31.5 μmol L^{-1}) of WHO in drinking water. In the second step the produced ensemble (PAR-Cu^{2+}), sensitively and selectively detected a low concentration of Cys via indicator displacement assay system. The detection limit for Cys was determined to be 72 nmol L^{-1}. The colorimetric detection operation is low-cost using PAR and copper ion and has a simple operation without any further modifications.[70]

The Fe^{3+}, Cu^{2+} and cysteine play important roles in many metabolic processes. Therefore, the selective and sensitive sensing of them is in ever-increasing demand for human health. The sensing of analytes through multi-responsive probes is a promising strategy. In the present study, a novel multi-responsive fluorescence probe (**AIP**) based on anthracene and isophorone units is reported. The structure of **AIP** was elucidated and its sensing properties were examined. **AIP** displayed a remarkable emission enhancing response for Fe^{3+} (LOD:87.3nM) and quenching for Cu^{2+} (LOD:30.1 nM) in the mixed aqueous medium with quick response times. Moreover, **AIP**- Cu^{2+}complex could selectively sense cysteine (LOD:0.25 μM) among other tested amino acids and anions. Test strips including **AIP** were produced for the detection of Fe^{3+} and Cu^{2+}, practically. Theoretical calculations indicated that ICT and MLCT processes are responsible for fluorescence sensing. The results demonstrated potential that the novel sensory **AIP** can be used as a multi-analyte fluorogenic probe toward Fe^{3+}, Cu^{2+} and cysteine [71].

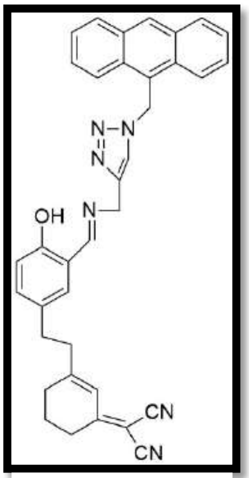


Figure 11. AIP

The copper and creatinine at normal conditions of pH and temperature was detected by PAQd. The turn on turn off sensor was highly efficient in detecting copper and creatinine in blood serum. It could also detect the intracellular and extracellular Cu^{2+} and creatinine in cellular environment. The selectivity of the developed sensor was also proven towards the analytes considered. A simple, mobile camera based quantification of creatinine from human blood has also been proven using paper strips of the quantum dot based sensor. Synthesis of such a sensor for detection of multianalytes will open up new horizon in the biomedical detection systems [72].

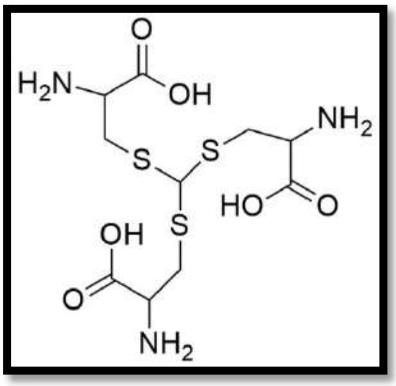


Figure 12. PAQd

The selected IPy/SDS system shows turn-off responses to Cu^{2+}, however, the quenching effect of Cu^{2+} can be increased by amino acids with high pI values such as arginine (Arg) and lysine (Lys). Therefore, the optimized ternary system based on IPy/SDS/ Cu^{2+} can function as a highly sensitive and selective fluorescent sensor for these two amino acids, displaying detection limits of 5.2 nM and 14.6 nM for Arg and Lys, respectively.[73]

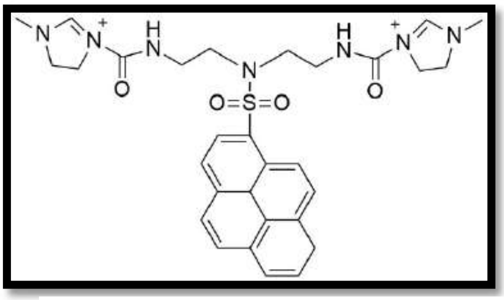


Figure 13. IPy

The detection of metal ions and amino acids by the aniline oligomer-based receptor has not been reported yet, to the best of our knowledge. In this study, an efficient multifunctional cation-amino acid sensor (CAS)with aniline moiety and chiral thiourea binding site was synthesized by the reaction of aniline trimer and (S)-(+)-1-phenyl ethyl isothiocyanate. CAS can sense Fe^{3+}, Cu^{2+}, Ag^{+} ions, and L-tryptophan. These results can be recognized by the naked eye. The appropriate pH range for the quantitative analysis of Fe^{3+}, Cu^{2+}, and Ag^{+} by CAS in DMSO water (30 vol% water) was evaluated.[74]

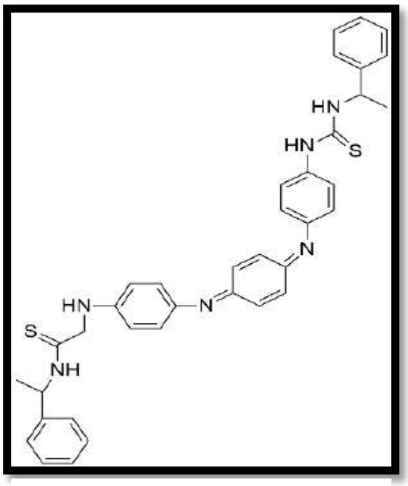


Figure 14. CAS

MATERIALS &METHODS

CHAPTER-II

MATERIALS, METHODS AND TECHNIQUES

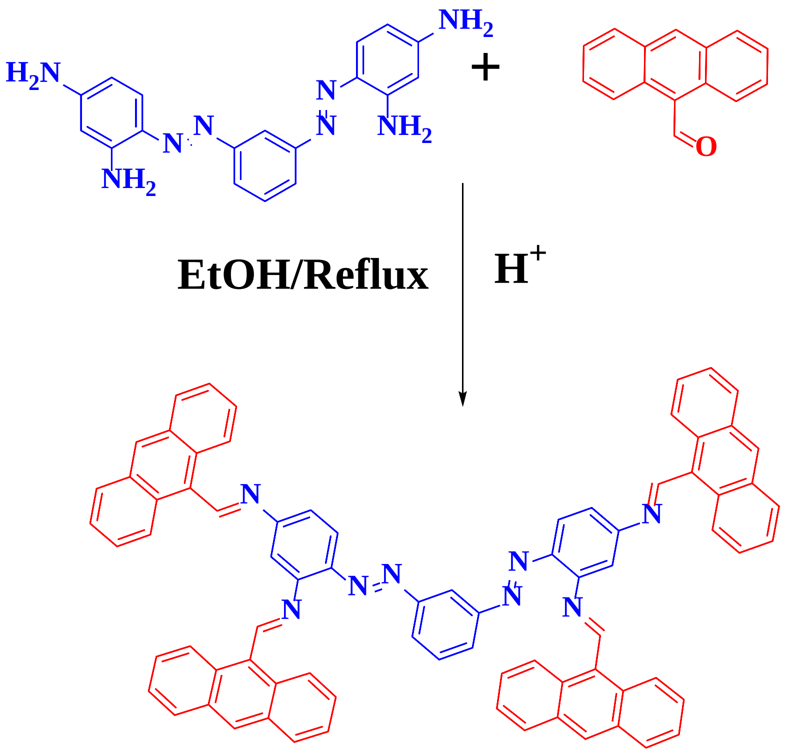
2.1 MATERIALS

Analytical grade solvents and double distilled water were used in all steps. Anthracene -1- carboxaldehyde (AA) purchased from AVRA chemicals and Bismarck brown yellow dye (BY), glacial acetic acid, methanol, ethanol and acetone were purchased from Sigma Aldrich chemical company.

2.2 EXPERIMENTAL METHODS

2.2.1. GENERAL PROCEDURE FOR THE SYNTHESIS OF (1E,1'E,1''E,1'''E)-N,N',N'',N'''-(((1E,1'E)-1,3-PHENYLENEBIS(DIAZENE-2,1-DIYL))BIS(BENZENE-4,1,3-TRIYL))TETRAKIS(1-(ANTHRACEN-9-YL)METHANIMINE) (BYAA).

To the 20 mL ethanolic solution of anthracene aldehyde [4.1 equivalent] and Bismarck brown yellow dye [1 equivalent], catalytic amount (200 µL) of glacial acetic acid was added as catalytic and then stirred in magnetic stirrer for 24 hours at reflux condition. The reddish-brown solid product was obtained and the reaction was confirmed through TLC (as single spot), then thoroughly washed with PET ether (90%), ethyl acetate (8%), ethanol (1%) and Methanol (1%). Following the completion of the purification, the formed solid was filtered and washed with cold EtOH. The product was dried for 10 hours in a hot air oven at 45 °C to produce reddish-brown solid **BYAA** in **Scheme 1** (54 mg, 40 %). The structure of compound was confirmed by FT-IR, and ^{1}H-NMR. Calculated mass = 1099.31g



(1*E*,1'*E*,1''*E*,1'''*E*)-*N*’*N*',*N*'',*N*'''-(((1*E*,1'*E*)-1,3-phenylenebis(diazene-2,1-diyl))bis(benzene-4,1,3-triyl))tetrakis(1-(anthracen-9-yl)methanimine)

Scheme 1. Reagent and condition to synthesize of ligand BBYAA

CHARACTERIZATION OF BYAA:

2.2.3 Functional Group Characterization by FT-IR Spectral Technique

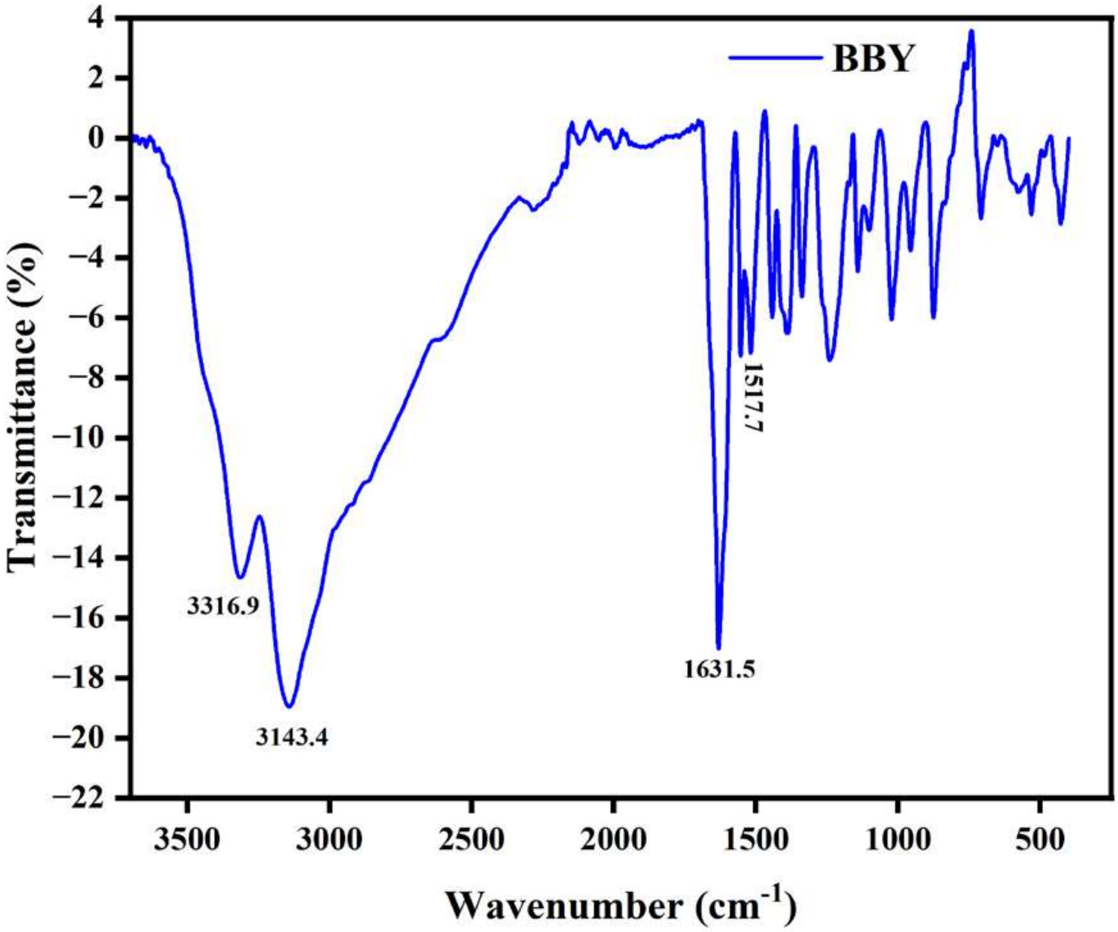


Figure.15. FT-IR Spectra of Bismarck brown yellow dye (BY)

Functional Group	**N–H stretching**	**N–H stretching**	**N=N Azo group**
Wavenumber (cm^{-1})	3316.9	3143.4	1517.7, 1631.5

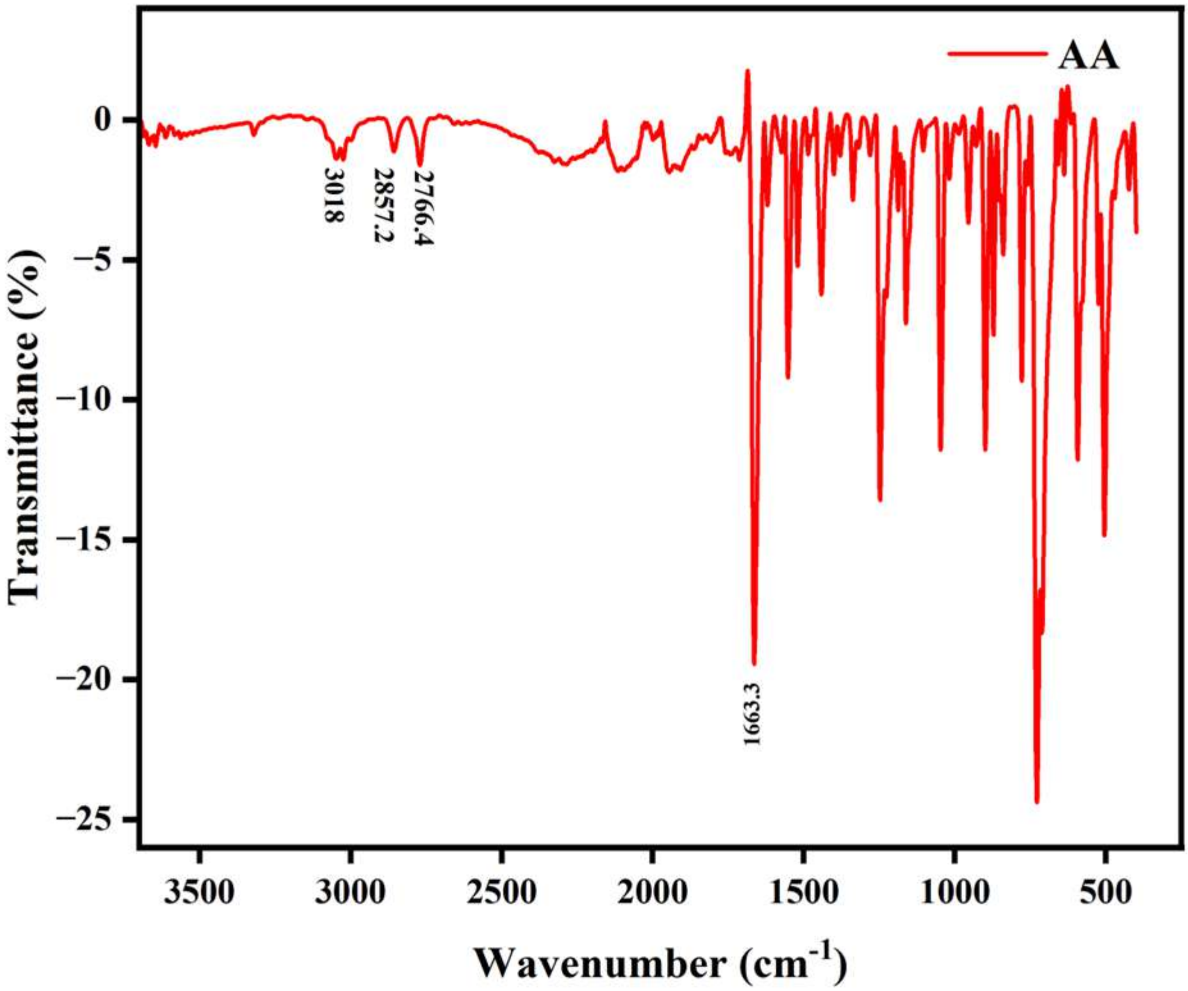


Figure. 16. FT-IR Spectrum of Anthracene -1- carboxaldehyde (AA)

Functional Group	**sp^2 C-H stretching**	**C-H stretching**	**C-H stretching**	**Aldehyde C=O Stretching**
Wavenumber (cm^{-1})	3018	2857.2	2766.4	1663.3

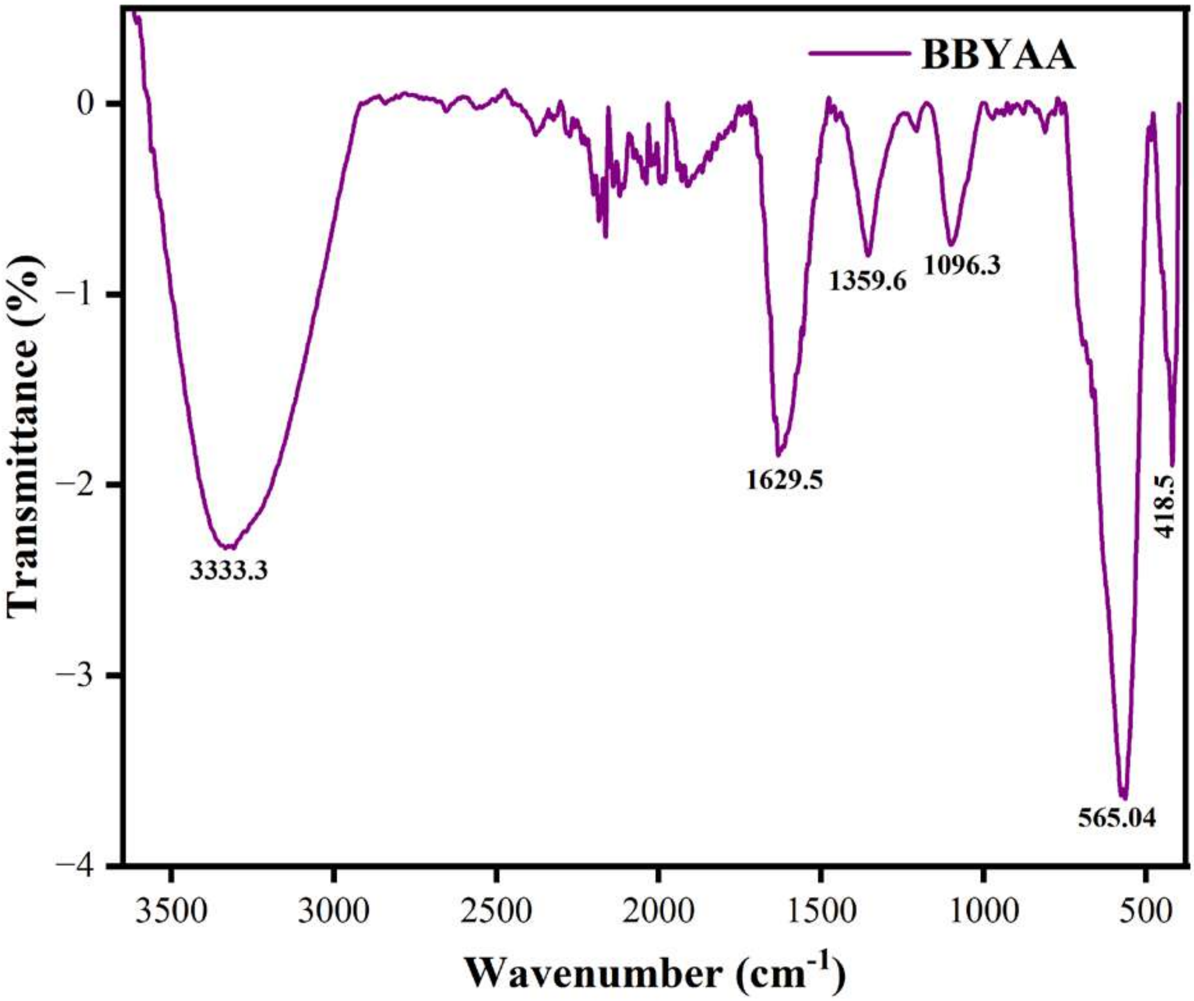


Figure. 17. FT-IR Spectrum of BY-AA ligand

Functional Group	**C-H Imine**	**C=N Imine**	**C=C Aromatic**	**C-N imine**	**N=N azo**
Wavenumber (cm^{-1})	3333.3	1629.5	1359.6	1096.3	Appx. 1509 marge with 1629

2.2.4 Structural Characterization by ^{1}H-NMR Spectral Technique

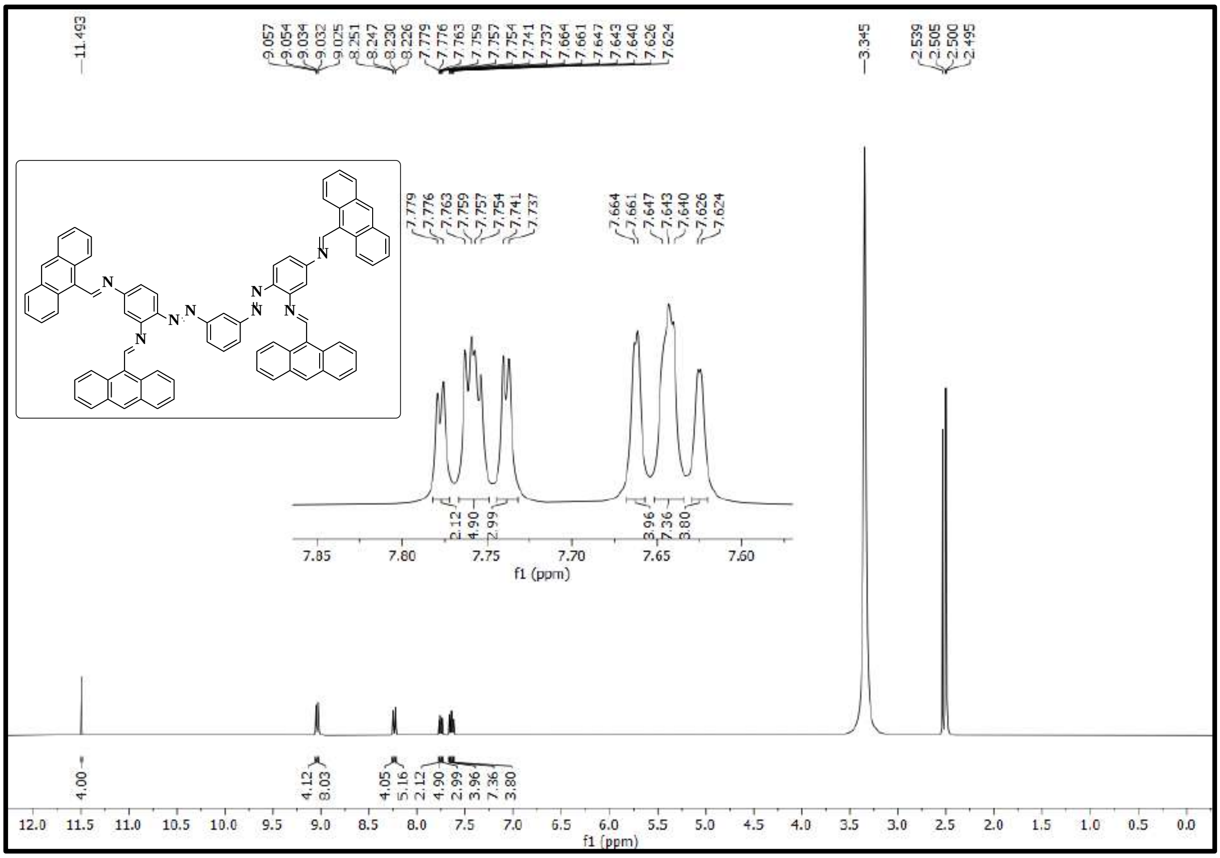


Figure. 18. The ^{1}H-NMR spectrum of BYAA ligand in DMSO-D_6

The ^{1}H-NMR (400 MHz, DMSO-D_6) spectrum of BYAA (**Fig. 18**): δ (ppm) 11.49 (s, 4H, -N=CH-), 9.05 (d, 4H), 9.03-9.02 (t, 8H), 8.25 (d, 4H), 8.22 (d, 5H), 7.77 (d, 2H), 7.76-7.75 (q, 5H), 7.74-7.73 (d, 3H), 7.66 (d, 4H), 7.64 (t, 7H), 7.62 (d, 4H), 3.34 and 2.50 (Water & DMSO-D_6). The ^{13}C-NMR (100 MHz, DMSO-D_6) spectrum of BYAA (Fig.): δ (ppm) 194.28 (-C=N), 135.28, 131.38, 129.37, 129.31, 125.88, 123.50.

RESULT AND DISCUSSIONS

3.1. SPECTROPHOTOMETRIC STUDY

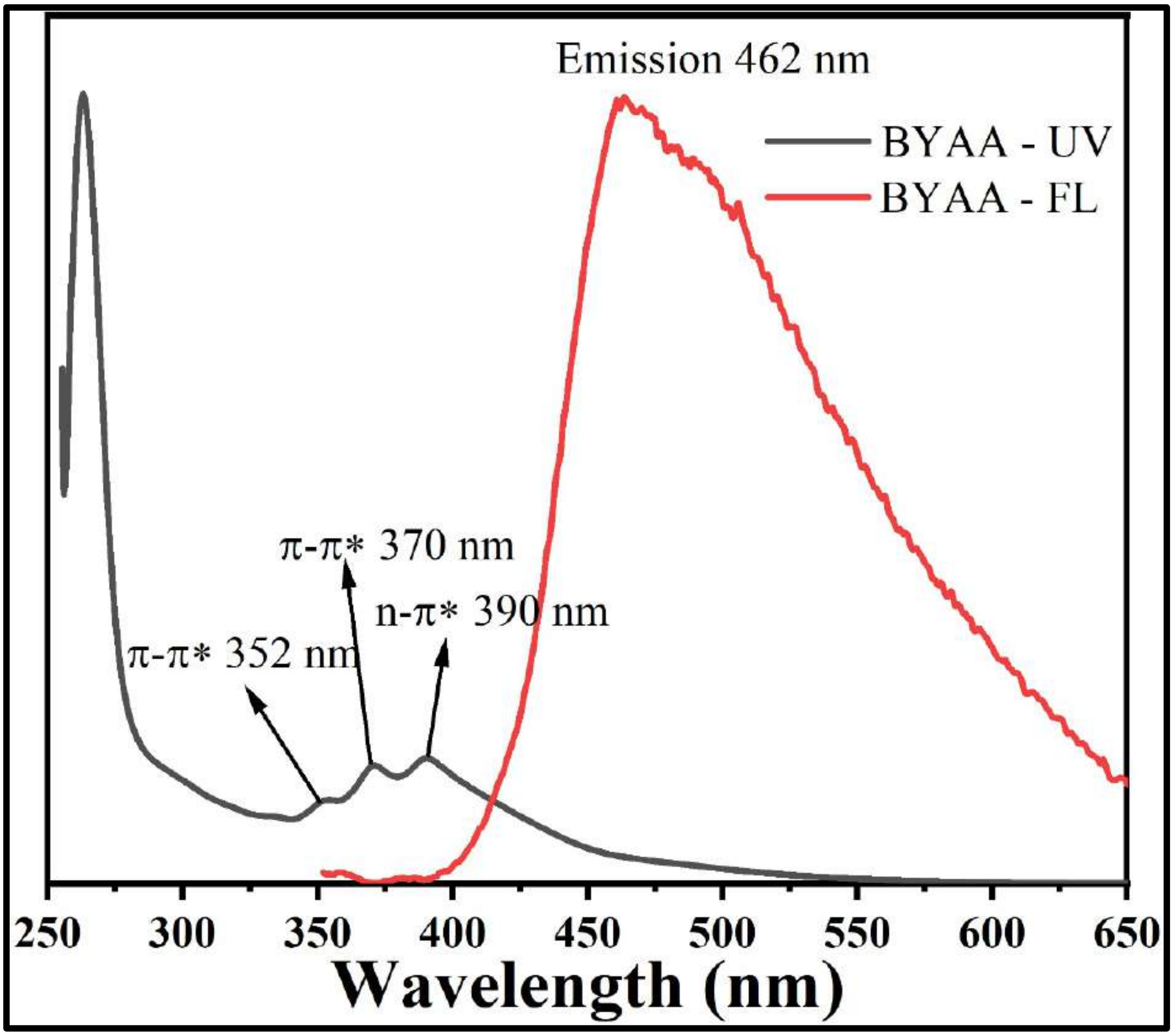


Figure19. Absorbance and Emission properties of BYAA ligand 50 µM in DMSO

At optimal experimental conditions, the BY-AA shows absorbance peak at 352 nm and 370 nm due to the occurrence of π-π* transitions for aldehyde and amine respectively. The peak at 390 nm due to the occurrence of n-π* transition. The UV spectroscopy analysis of BB-YY reveals prominent emission peak at 462 nm indicating the presence of specific emitter or chromophores and limited donor to acceptor electron transfer.

3.2. AGGREGATION INDUCED EMISSION (AIE) STUDIES:

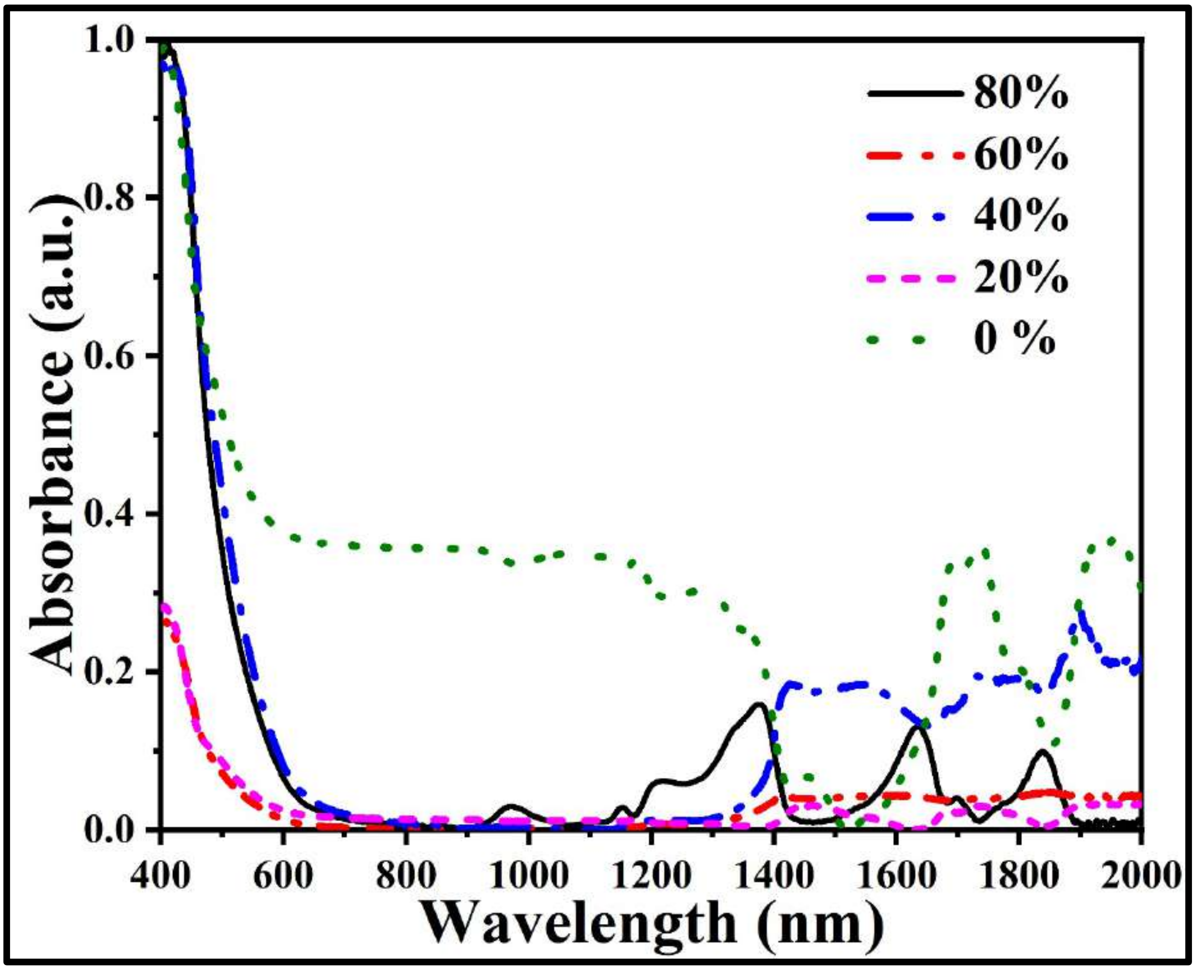


Figure 20. UV-NIR spectrum of BYAA ligand (50 µM) in DMSO:H_2O % solvent system from 0% H_2O to 80 % H_2O

UV-Vis studies were thoroughly examined for synthesized BY-AA under different experimental condition. The BY-AA ligand (50µM) in DMSO: H_2O system subjected to UV-NIR spectra in which the absorbance peaks were evolved at 966 nm, 1200 nm, 1374 nm, 1636 nm at 20% to 80% (DMSO:H_2O) solvent system is shown in Fig.20 this indicates that BY-AA ligand is active in the NIR region at 20%:80% (DMSO:H_2O) solvent system. These peaks are obtained in NIR region due to growth of microcrystalline from solution phase by adding of co-solvent of H_2O in DMSO.

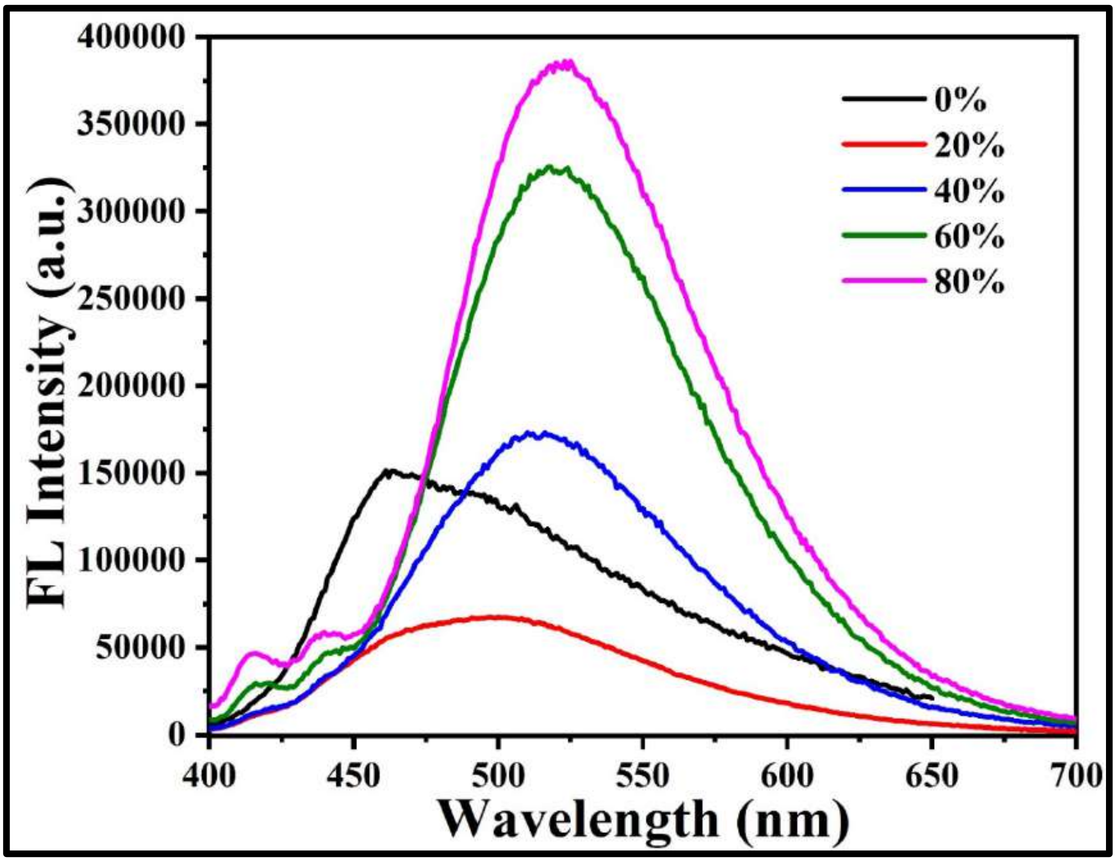


Figure.21. Emission spectrum of BYAA ligand in DMSO:H_2O % solvent system from 0% H_2O to 80 % H_2O

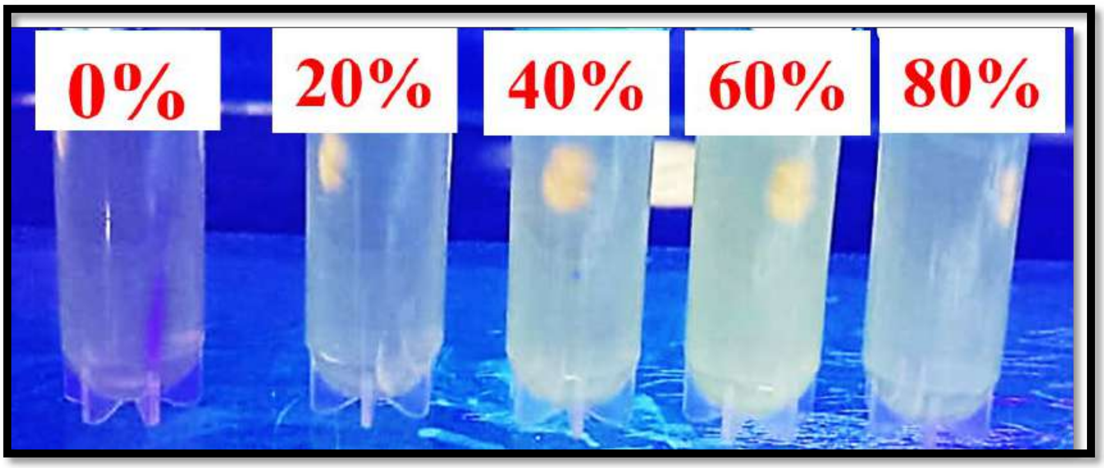


Figure 22. Photo image of BYAA ligand under UV light in DMSO:H_2O % solvent system from 0% H_2O to 80 % H_2O.

The probe BY-AA shows strong fluorescence emission under two phases, solution and solid-state emission, in a mixture solution DMSO:H_2O. In Fig. 21 BY-AA (50 µM) shows emission at 462 nm in DMSO. Under similar conditions, the fluorescence ability of BY-AA was verified in the absence and presence of water by excitation at 370 nm, when increasing the water up to 80%. The spectral studies reveal that BY-AA in DMSO:H_2O solvent binary mixtures exhibit a substantial redshift fluorescence enhancement at 524 nm from 20% to 80%. The emission intensity was shifted from 462 nm to 524 nm due to AIE by inhibition of intramolecular rotation, π-π stacking of self-assembly, and reduced non-radiative decay. The recognition capability to examine the AIE of BY-AA, the naked-eye visible color changes of BY-AA is studied in the presence of UV light. The fluorescence enhancement of BY-AA was observed in 20 to 80% DMSO:H_2O solvent mixtures (Fig. 22). Since the BY-AA is nominated as an AIEgen in 80% DMSOH_2O solvent mixtures.

3.3. SELECTIVITY AND SENSITIVITY

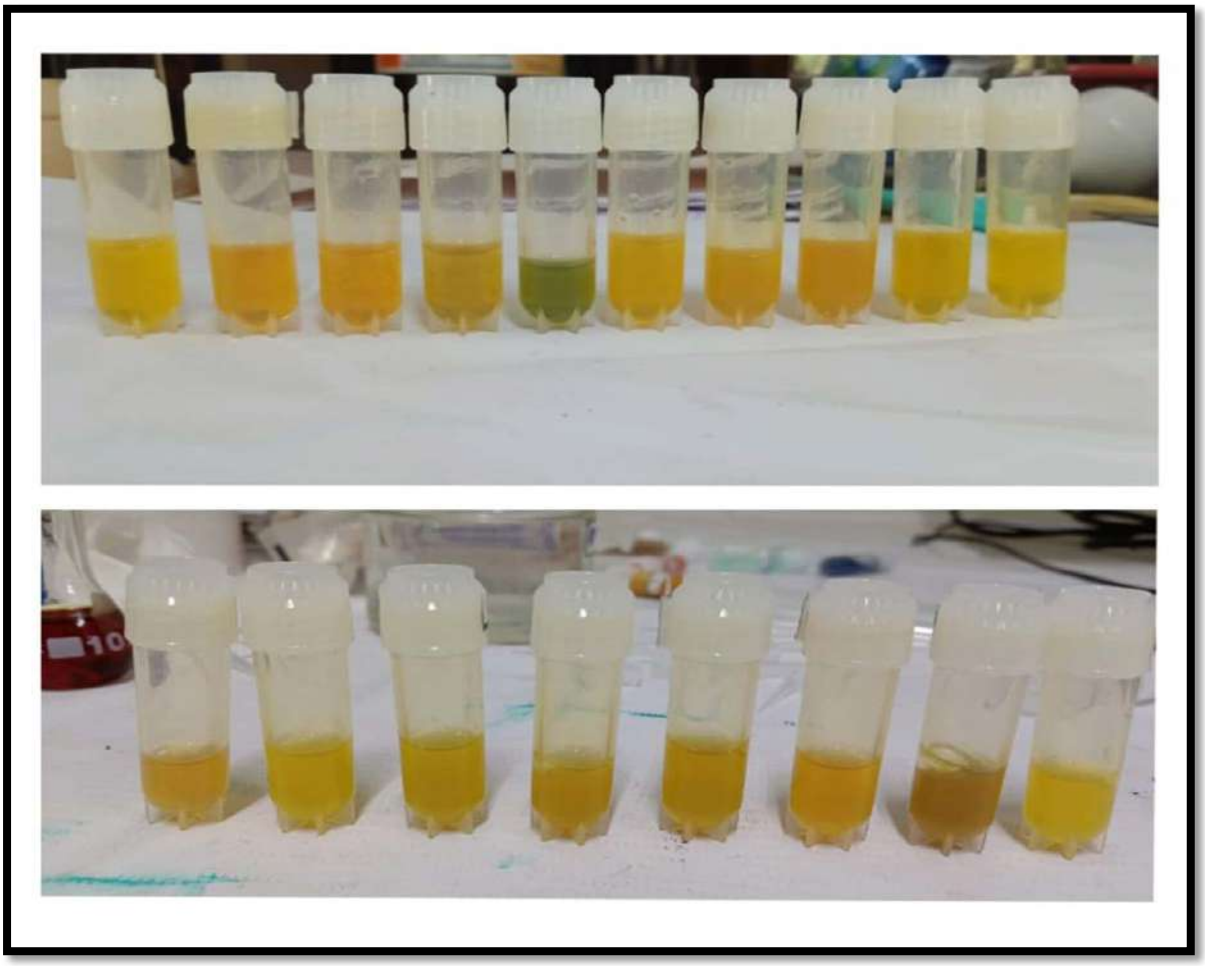


Figure 23. Changes in the absorption of BY-AA induced by various metal ions (4.0 equiv.) in DMSO:H_2O (9:1 v/v). Blank, including Fe^{3+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Al^{3+}, Cr^{3+}, Ca^{2+}, Zn^{2+}, Sn^{2+}, K^{+}, Ag^{+}, Hg^{2+}, Ba^{2+}, Mn^{2+}, Mg^{2+}, Cd^{2+}, and Pb^{2+}.

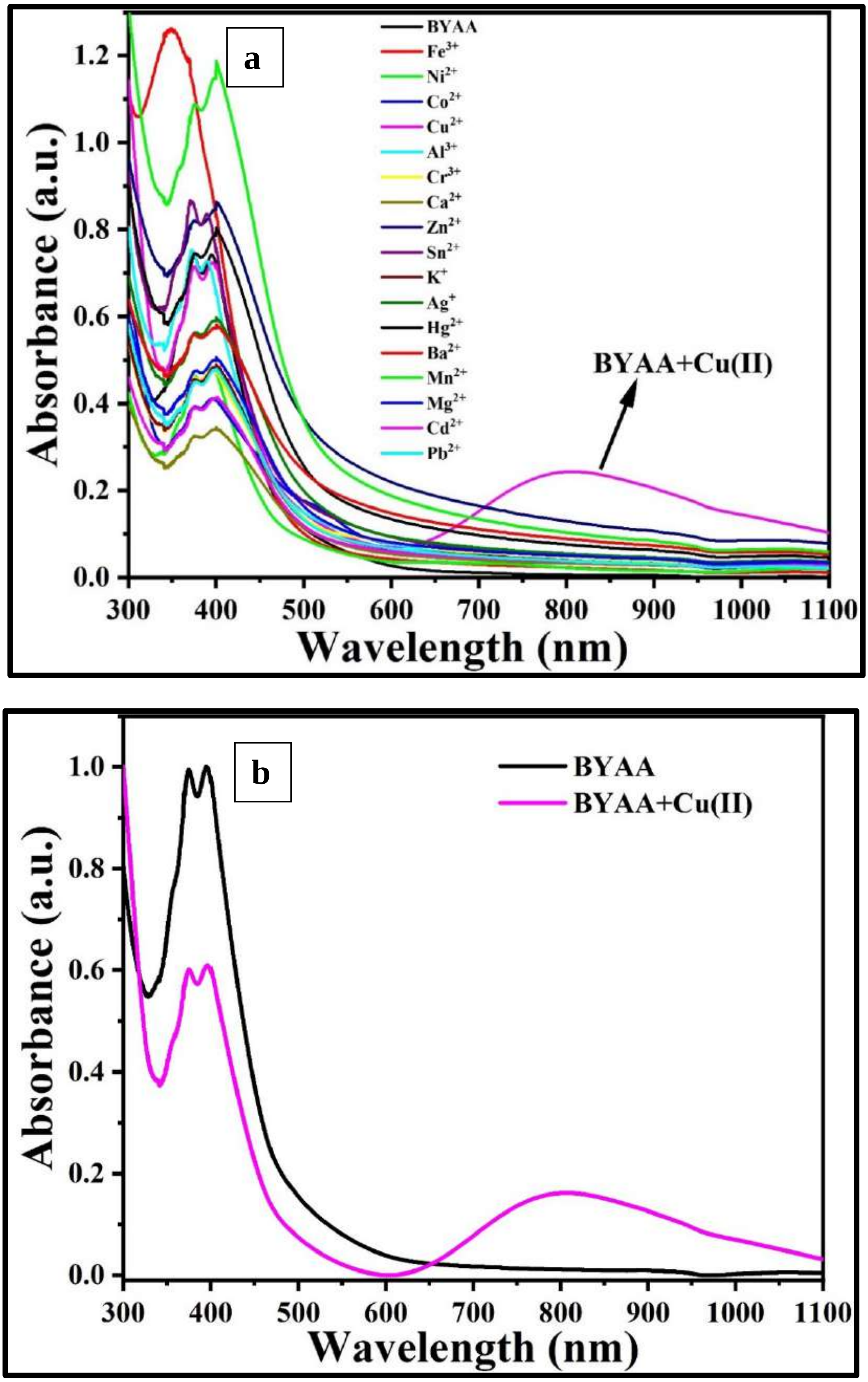


Figure 24. UV-Visible spectral response of BYAA ligand (25 µM) with (0.1 mM) of various metal ions, (b) UV-Visible spectral response of BYAA ligand (25 µM) in the presence of Cu Cu^{2+} (100 µM) in DMSO: H_2O (9:1, v/v) media.

An initial study was carried out in the solution phase utilizing the spectrophotometric technique and solvent medium DMSO: H_2O (9:1, v/v). Various metal ions were used to determine the selectivity of BY-AA AIEgen (25 µM) and the visible color changes of BY-AA AIEgen in the presence and absence of metal ions (4 equiv.) Such as, Fe^{3+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Al^{3+}, Cr^{3+}, Ca^{2+}, Zn^{2+}, Sn^{2+}, K^{+}, Ag^{+}, Hg^{2+}, Ba^{2+}, Mn^{2+}, Mg^{2+}, Cd^{2+}, and Pb^{2+}, by under Visble light. The noticeable color change (from yellow to green) of BY-AA AIEgen was observed only Cu^{2+} (Fig. 23), resulted in a remarkable colour change in the naked eye detection. Other tested metal ions did fail to produce such a change.

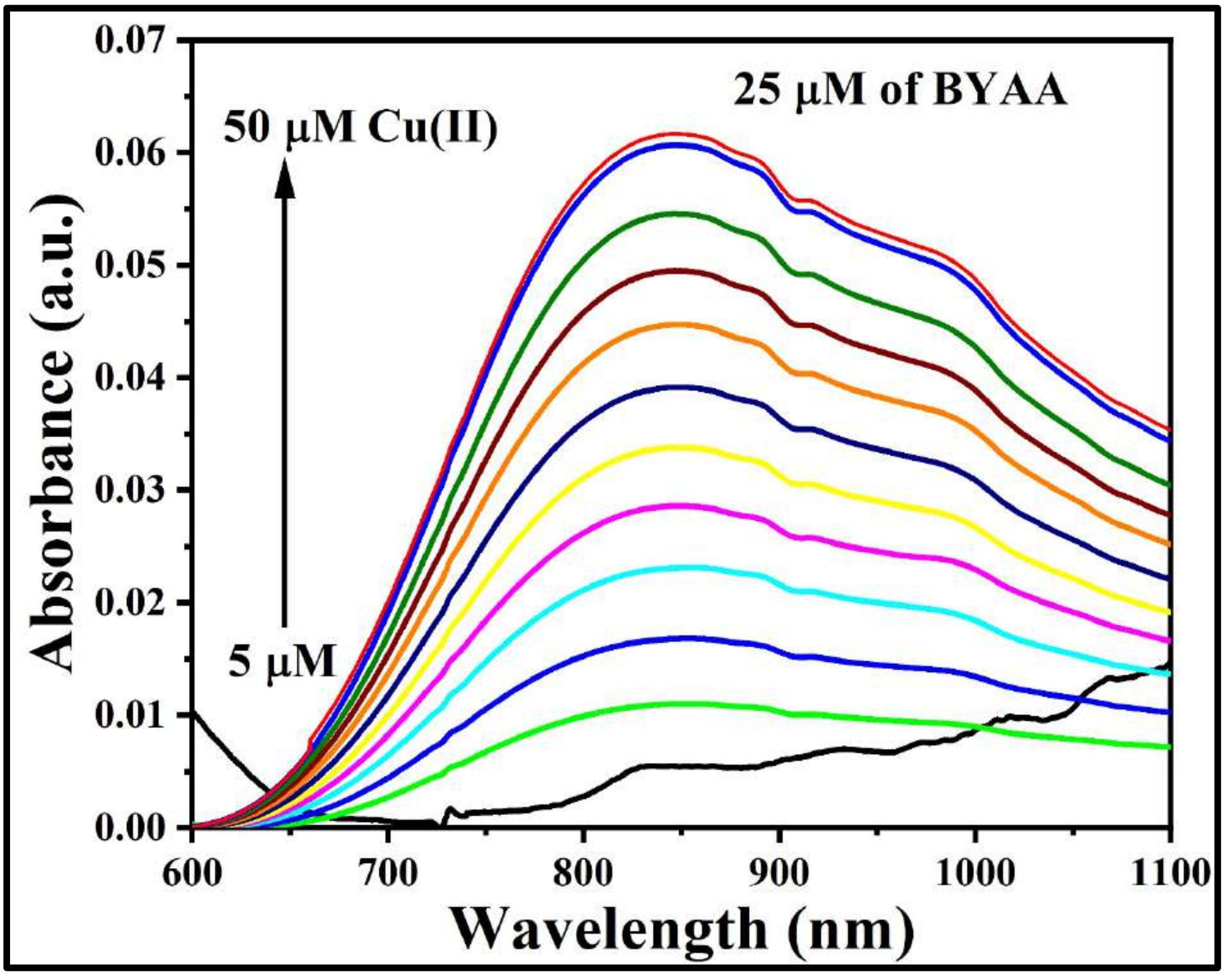
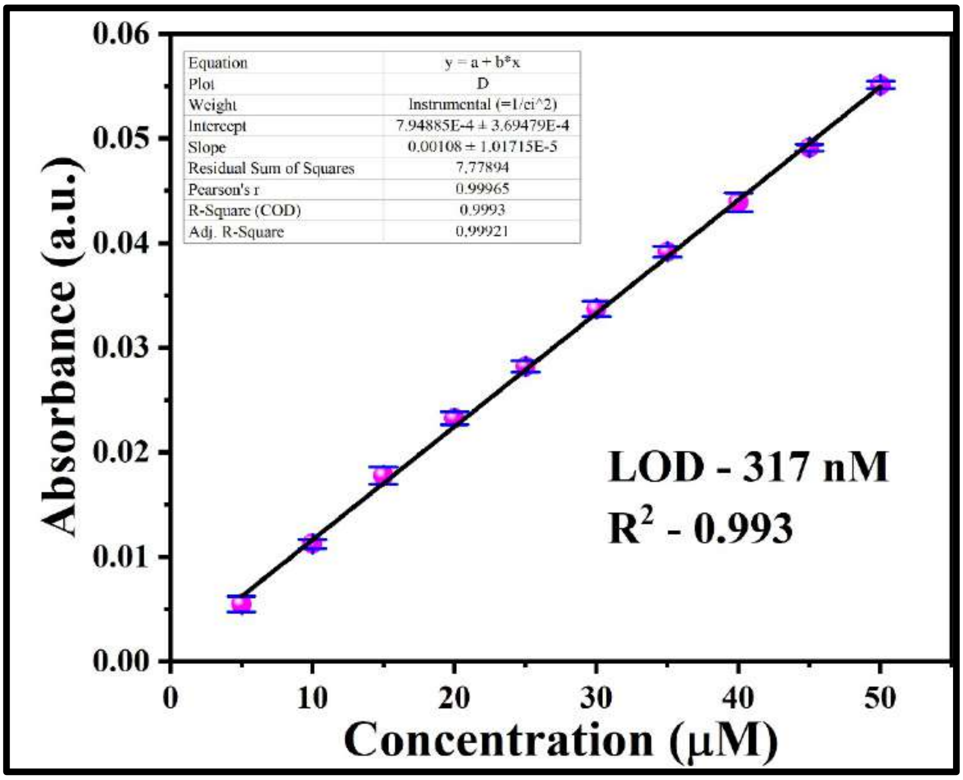


Figure 25. UV-vis spectra titration of BYAA ligand (25 μM) in the presence of varying concentration of Cu $^{2+}$ (0–50 μM) in DMSO: H_2O (9:1, v/v) media.

In the presence and absence of various metal ions, the U.V. spectrum of BY-AA AIEgen was verified under similar conditions. As seen from **Fig. 24a**, BY-AA AIEgen alone exhibits two types absorbance band of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ appeared at 352 & 370 and 390 nm, respectively. After the interaction of BY-AA AIEgen with Cu metal ion (**Fig. 24b)**, decreases the 352 & 370 and 390 nm peaks. The addition of Cu^{2+} to BY-AA AIEgen new absorption bands is obtained at 845 nm. At 845 nm response of BY-AA AIEgen to Cu^{2+} metal ions, To the visible region

A calorimetric study was conducted to detect the presence of copper ions using a ligand BY-AA (25 μM) in DMSO: H_2O (9:1, v/v) media and Cu(II) (0-50 μM) solution. The systematic addition of Cu(II) to BY-AA AIEgen results in the systematic development of the new absorbance band at 845 nm while decreasing the absorbance bands at 352 & 370 and 390 nm. (**Fig. 24b**). As a result, the chelation between Cu(II) metal ions and ligand BY-AA AIEgen is assessed as the preferential colorimetric response of BY-AA AIEgen towards Cu(II). The appearance of the new absorption band at 845 nm after the addition of Cu(II) metal ion to

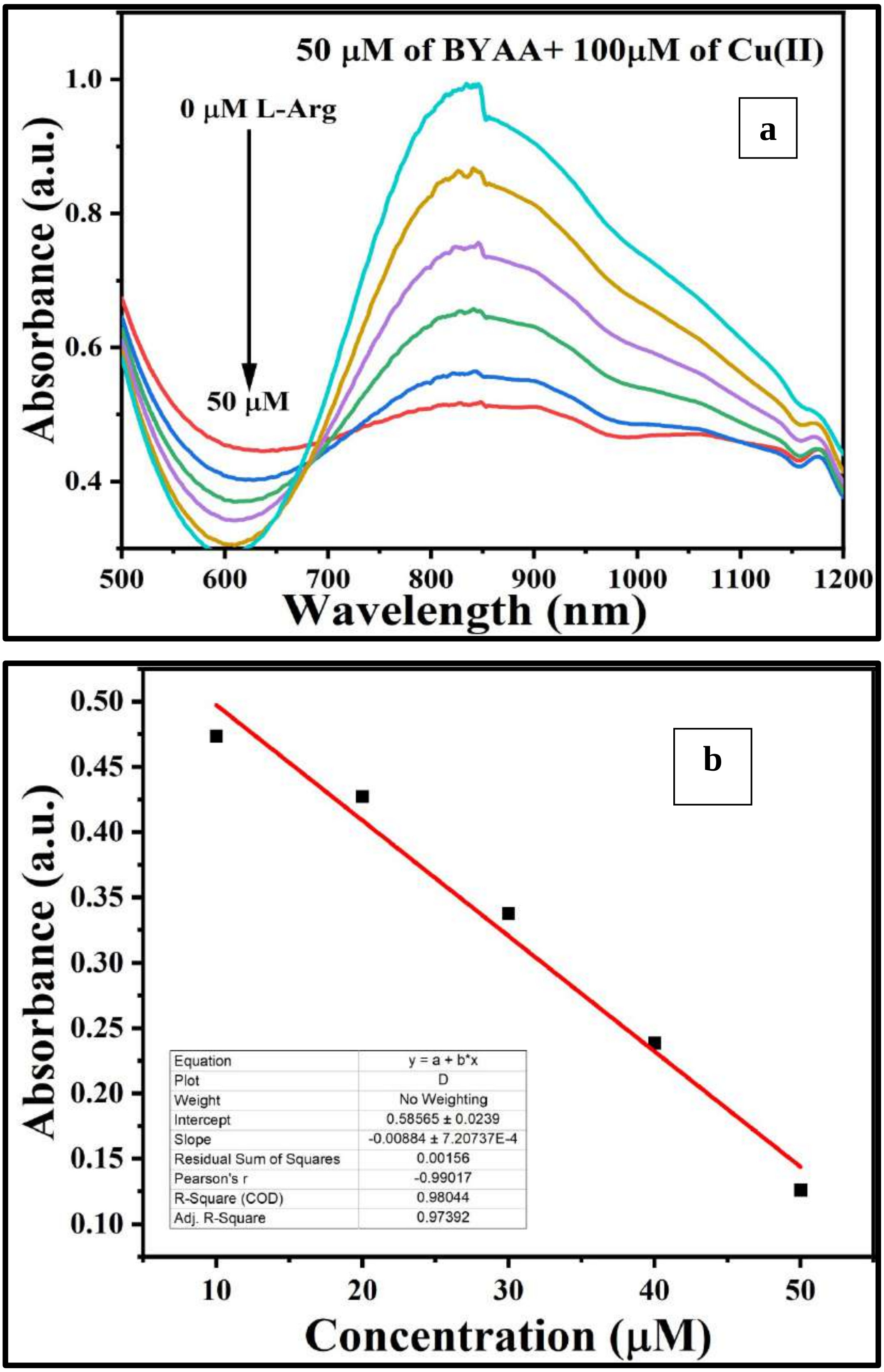
BY-AA AIEgen is attributed to the coordination of Cu(II) to the nitrogen atoms of the -N=N- azo moiety and the nitrogen atoms of the Schiff base (BY-AA AIEgen) moiety. The absorbance band at 845 nm has been observed in particular complexes and ascribed to the ligand-metal charge transfer transition in BY-AA AIEgen between Cu(II) metal ions. However, BY-AA AIEgen exhibited no discernible spectrum responses to other metal ions, indicating that BY-AA AIEgen is very selective to Cu(II).



Equation	y = a + b*x
Plot	D
Weight	Instrumental (=1/ci^2)
Intercept	7.94885E-4 ± 3.69479E-4
Slope	0.00108 ± 1.01715E-5
Residual Sum of Squares	7.77894
Pearson's r	0.99965
R-Square (COD)	0.9993
Adj. R-Square	0.99921

Figure 26. Calibration curve of Cu(II) using BY-AA AIEgen

The titration spectral data show a linear relationship between Cu(II) molar concentrations and observed emission intensity in the range of 0 to 50 M (**Fig. 15**). The limit of detection (LOD) of Cu(II) using the BY-AA AIEgen probe is calculated from the calibration curve of absorbance incremental addition titration. According to the IUPAC method, the LOD is calculated (LOD = 3σb/slope), where the slope is obtained from the calibration curve and σb is the standard deviation of the absorbance intensity of BY-AA. The limit of detection (LOD) of Cu(II) using BY-AA AIEgen is obtained using the fluorescence titration calibration curve. The IUPAC approach calculates. The results indicate that the LOD of Cu(II) are 317 µM.



Equation	y = a + b*x
Plot	D
Weight	No Weighting
Intercept	0.58565 ± 0.0239
Slope	-0.00884 ± 7.20737E-4
Residual Sum of Squares	0.00156
Pearson's r	-0.99017
R-Square (COD)	0.98044
Adj. R-Square	0.97392

FIGURE 27. UV-vis spectra titration BYAA+Cu(II) complex in presence of various concentration of L-Arginine DMSO:H_2O, b) Calibration curve of L- L-Arginine using BY-AA+Cu(II) complex

To demonstrate the multi analyte sensing ability of BYAA, different known concentrations of arginine and Cu were added to 100µM of the same. In the presence of arginine, emission peak showed concentration dependent fluorescence enhancement. The sensor (50µM of BY-AA) could detect arginine (Fig. 27 a). Similarly, upon Cu addition to 50µM of BY-AA, the fluorescence quenching of the takes place. Thus, in principle, BY-AA acts as a turn-on turn-off sensor for arginine and copper, respectively based on the fluorescence enhancement and quenching, i.e. BY-AA, with different excitations can simultaneously detect both analytes with corresponding enhancement.

CONCLUSION

CONCLUSION

- ✓ A novel (1e,1'e,1"e,1'"e)-n,n',n",n'"-(((1e,1'e)-1,3-phenylenebis(diazene-2,1-diyl))bis(benzene-4,1,3-triyl))tetrakis(1-(anthracen-9-yl)methanimine) **(BYAA) were** synthesized and characterized thoroughly by ^{1}H-NMR and IR techniques.

- ✓ The spectral properties of BY-AA was studied thoroughly using UV-Vis and spectrofluorometry techniques.

- ✓ The sensing property of the compound was tested for different types of metal ions like Fe^{3+}, Ni^{2+}, Co^{2+}, Al^{3+}, Cr^{3+}, Ca^{2+}, Zn^{2+}, Sn^{2+}, K^{+}, Ag^{+}, Hg^{2+}, Ba^{2+}, Mn^{2+}, Mg^{2+}, Cd^{2+}, and Pb^{2+} ions.

- ✓ BY-AA has showed a high selectivity towards the Cu^{2+} ions.

- ✓ As a colorimetric sensor it could detect Cu^{2+} ions with the LOD of 317 µM.

- ✓ The developed colorimetric has initially adapted MLCT mechanism and possess AIE property.

- ✓ BY-AA and Cu^{2+} complex senses the arginine amino acid. In future the sensitivity and selectively will be studied.

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