In vitro DNA Binding Studies of Selected Heterocyclic Compounds and their Photovoltaic Applications

AKHILA.C
13PCH001

Dissertation submitted to
Avinashilingam Institute for Home Science and
Higher Education for Women
(University Estd. u/s 3 of UGC Act 1956)
Coimbatore-641043, Tamil Nadu, India

In partial fulfilment of the requirements for the
Master's Degree in Chemistry
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Supervisor

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Signature of the
Head of Department

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CONTENTS

CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS AND ACRONYMS

2-AAP	2-Aminoacetophenone
4MVQ	4-methyl 3-vinyl quinolone-2(1H)-one
2CMVQ	2-chloro-4-methyl-3-vinyl quinolines
4MVQT	4-methyl-3-vinylquinoline-2(1H) thiones
DMTQ	2, 3-dihydro-4-methyl-thieno(2,3-b) quinoline
DDDS	4-methyl-3-vinyl quinoline-2(1H)-thiones to 2,2’-(4,4-dimethyl-3,3’-divinyl)disulphide
ABP	2-Aminobenzophenone
4PVQ	4-phenyl 3-vinyl quinoline-2(1H)-one
2CPVQ	2-chloro-4-phenyl-3-vinyl quinoline
4PVQT	4-phenyl-3-vinylquinoline-2(1H)-thiones
ACBP	2-Amino-5-chlorobenzophenone
6CPVQ	6-chloro-4-phenyl 3-vinyl quinolone-2(1H)-one
DCPVQ	2,6-Dichloro-4-phenyl-3-vinyl quinoline
ANBP	2-Amino-5-nitrobenzophenone
6NPVQ	6-Nitro-4-phenyl 3-vinyl quinoline-2(1H)-one
6NCPVQ	6-nitro-2-chloro-4-phenyl-3-vinyl quinoline
6NPVQT	6-Nitro-4-phenyl-3-vinyl quinoline-2(1H)-thiones
FTO	Fluorine-doped tin oxide
Ct	Calf Thymus
DNA	Deoxyribonucleic acid
ds	Double strand
DSSC	Dye sensitized solar cell
λ_{max}	Maximum wavelength
µl	Micro litre
V	Volatage
µA	Micro gram
mg	Milligram

HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
M	Molar
%	Percentage
et al	And all
OD	Optical density
UV	Ultra violet
nm	Nano metre

INTRODUCTION

1. INTRODUCTION

Organic compounds have variety of applications in daily life. Heterocyclics are a class of compounds which play a characteristic role in our daily life. They have variety of applications in the field of agricultural, pharma and industry. Heterocyclics include oxygen, nitrogen, sulphur groups. Quinolines are one such class of nitrogen compounds with wide number of pharmaceutical applications. Streptonigrin and lavendamycin are highly substituted quinolines-5,8-dione antitumor antibiotics which have activities against a broad range of tumors (**Balitz et al.,1982**).

Quinoxalines and quinolone derivatives have always being of great interest in medicinal chemistry because of their broad spectrum of biological activities such as antihistaminic, antitrypanosomal, anti-herpes, anti plasmodial (**Refaat et al.,2004;Urquiola et al.,2006;Harmenberg et al 1998;Zarranz et al.,2006**).

On viewing the tremendous properties of Quinolines, it was felt essential to take up organic synthesis and explore its applications. With this aim in this present work quinolinones, substituted quinolinones, thiones, have been synthesized.

The quinolines, substituted quinolines, thiones have also medicinal applications such as anti-bacterial, anti-fungal, anti-mutagenic (**Lalitha et al.,2010**). As they have variety of biological applications it is anticipated to have good interaction with DNA. DNA is a pharmacological target of many of the drugs that are currently in clinical use. Targeting DNA to regulate cell functions by modulating transcription or by replication seems logical. Small ligand molecules act as drug when alteration or inhibition of DNA function is required to cure or control a disease (**Kennard,1993**).

In this present work the *invitro* DNA binding studies of quinolinones, substituted quinolines, thiones has been attempted. The binding interactions could be studied by numerous methods including UV-Visible spectroscopy, fluorescence spectroscopy, X-ray diffraction, surface morphology test, and cyclic voltammetry techniques (**Coates et al., 1996; Zhao et al., 1999; Wang et al., 2003**). In this study UV spectroscopic studies was carried out and the interaction of the DNA with synthetic compounds was studied.

The binding of DNA to drug can affect its transcription, replication, the expression of genetic information in cells, and thereby influence its physiological function. Drug-DNA interaction studies have been carried out to obtain the effective information and explain the disease mechanism. The different binding studies have always been widely used in designing low toxic drug for clinical use (**Singh et al., 1992**) .

The DNA used for this study is calf thymus DNA (CtDNA). Calf thymus DNA (ct-DNA) is a low protein and highly polymerized nucleic acid. The investigation of drug–DNA interaction is important for understanding the molecular mechanism of drug action. The possible interaction model between small molecules and DNA generally follows three models:

(i) electrostatic binding between positively charged species and negative charged DNA phosphate,
(ii) groove binding in which a molecule is bounded in the groove of DNA involving hydrogen bonding, the Van der Waals interaction force and
(iii) intercalative binding between the drug and base pairs(**Hartwig et al., Mantle et al, Jang,2010**)

The clarification on the binding mechanism of these stains to biological macromolecules could help us to understand the biological value and toxicity of them (**Qingxiang Wang et al.,2011**).

In this study the interaction of ct-DNA with synthetic compounds was analyzed using UV-Visible spectroscopy. It is on the basics of two criteria such as time variation and concentration variation. The UV-Visible spectroscopy is simplest and most commonly employed instrumental technique for studying the interaction of drug with DNA. The study can be carried out by monitoring the changes in absorption properties of either the compound or drug. Here the variation in concentration of compound has been carried out.

Apart from the pharma applications, quinolines exhibit good fluorescence property. They show good fluorescence in UV region in the electromagnetic spectrum. This property paved the way for the designing of the photovoltaic cells. This is actually the key link between the organic compounds and their application towards industry.

Energy problem will be the top one of the 10 critical problems that humans may face in the coming 50 years, which was pointed out by Professor Smalley of Rice University in the USA(**Hamakawa , 2002**). Although there are many sources of energy, solar energy is one of the ultimate sources which can be effectively used for the generation of electricity.

Solar cell converts solar energy into usable amount of direct current. Many attempts have been made by several researchers to prepare solar cells of higher efficiency. Solar cells can be of different types-dye sensitized, quantum dot, polymer. Long lasting solar cells have always been a challenge to scientists.

Dye Sensititzed Solar Cell (DSSC) is a new type of solar cell invented by professor Graetzel using bis(bipyridyl) Ru(II) complexes as a sensitizer to sensitize the TiO_2 thin film. It was found that such solar cell could reach to 7%, from which the era of the DSSC came to a threshold. High-temperature treatment, advanced equipment, high vacuum, and materials of high purity are not required. As a result, the cost of it is just 1/3–1/5 of that of the silicon solar cell. Moreover, DSSC has some characteristics that silicon does not have. According to preparation condition, it can be made transparent or colorful and also can be made as a flexible solar cell. The world record of the efficiency for DSSC has been raised up to over 11% (**Graetzel et al.,2006**), which is higher than that of amorphous silicon solar cell.

Dye Sensitized Solar Cell is made of low cost materials and do not need elaborate equipment to manufacture. Due to the high performances and low cost of production, DSSCs have become one of the most promising alternatives to the conventional solid silicon-based solar cells for the photovoltaic conversion of solar energy. Dye serves as the light absorber in DSSC whose properties decide the ability to create electrons and photoelectric conversion efficiency. As the most important part in DSSC, many requirements should be met. To obtain high photocurrent, the absorption spectrum of dye should be wide enough. It should also be firmly grafted to the oxide surface and inject the electrons to conduction with a high quantum efficiency. In addition, the dye should also be very stable when exposed to constant light irradiation (**Hong LIN et al.,2009**).

Dyes are efficient converting absorbed photons into free electrons in the TiO_2 .It has higher efficiency in higher temperature. A dye-sensitized solar cell is a low-cost solar cell belonging to the group of thin film solar cells(**Grätzel et al, 2004**). Natural dyes as well as organic dyes can be used as dye in the DSSCs. Natural dyes obtained from plant parts, fruits and vegetables are used as dyes. So far, many efficient organic dyes have been obtained, the highest efficiencies (η) of power conversion of DSSCs devices has achieved above 10%(**Zeng et al, 2010, Qin et al, 2008, Horiuchi et al., 2004,Koumura et al., 2006, Snaith et al, 2009**).

Dye serves as the light absorber in DSSC whose properties decide the ability to create electrons and photoelectric conversion efficiency. As the most important part in DSSC, many requirements should be met. To obtain high photocurrent, the absorption spectrum of dye should be wide enough. It should also be firmly grafted to the oxide surface and inject the electrons to conduction with a high quantum efficiency. In addition, the dye should also be very stable when exposed to constant light irradiation (**Nazeeruddin Md et al,1999**).

Nowadays, many kinds of metal-free organic dyes, such as coumarin, triarylamine, indoline , hemicyanine , merocyanines, squaraine ,benzothiadiazole, boradiazaindacenes, porphyrin, cyanine, perylene, azulene, and other oligothiophene dyes are being intensively investigated because of their facile design and synthesis, convenient control of absorption wavelength and lower cost. The performance of DSSCs based on organic dyes has recently been remarkably improved; however, their efficiency, ranging from 4-9%, still lags behind the efficiency of Ru complexes (**Hara et al.,2001;2003;2005; Wang et al.,2007;Hagberg et al.,2006;2008; Kim et al.,2006; Liang et al.,2007; Zhou et al.,2008; Qin et al.,2007; Justin Thomas et al., 2007; Horiuchi et al.,2003;2004**).

Considering the aforesaid need for fabricating solar cells with better efficiency and to exploit the fluorescent property of the synthesized organic heterocyclic compounds , it has been endeavored in this research work to utilize the compounds as dyes for solar cell fabrication.

1.1Objectives of the study

The present work on "***In vitro* DNA Binding Studies of Selected Heterocyclic Compounds and their Photovoltaic Applications**" has been carried out with following objectives

Phase I

- To synthesize quinolinones and their derivatives using microwave assisted method.
- Characterization of synthesized compounds
- *In vitro* DNA binding studies of synthetic compounds with calf-thymus CT DNA
- To analyze the mode of binding of ct-DNA with the synthesized heterocyclic compounds

The objectives of the phase 2 includes,

☼ Preparation of synthetic compounds as dye for DSSC.

☼ To fabricate economic Dye-Sensitized Solar Cells (DSSC)

☼ To calculate the current density and current voltage of the fabricated DSSC's

REVIEW OF LITERATURE

2. REVIEW OF LITERATURE

The review of literature related to microwave assisted synthesis of compounds, DNA binding studies and the fabrication of solar cells are given in the following pages.

2.1 Microwave assisted synthesis

Microwave has been applied in various fields and processes such as heating, sintering, drying, waste treatments, etc. In the medicinal industry, microwave has been used in various applications including breast cancer detection in humans, clinical microwave thermotherapy and proteomics. Microwave radiation has been used in chemical analysis and chemical synthesis. Microwave heating under controlled conditions offers distinct advantages over conventional heating. The reactions can be carried out in environmentally clean and safe solvents and in many cases reactions can be carried out under solvent-free conditions. The application of microwave methodology to chemical synthesis has opened up new opportunities for the synthetic chemists by providing novel routes not practical by conventional methods. **The application of microwave assisted synthesis in the medicinal and pharmaceutical industries will be emphasized in this review.**

Microwave assisted reactions are successfully applied in synthesis of nano materials, biochemical reactions, medicinal and pharmaceutical industries.Microwave assisted organic reactions using domestic or commercial ovens, basically known as MORE (Microwave Induced Organic Reaction Enhancement) Chemistry, is increasingly important. The MW-assisted chemical synthesis encompasses the syntheses of organic materials, organometallic compounds, coordination compounds, intercalation com- pounds, ceramic products, polymer products, solid-state compounds, and radiopharmaceuticals.

It has been found that microwave assisted reactions are found to be rapid, efficient and safe. The approach is eco-friendly and this pollution preventive strategy is now an important part of modern Combinatorial and Green Chemistry.Recent synthetic studies on various processes by utilizing MW irradiation have shown the high potential of microwave irradiation in obtaining high yield products. The experimental procedures are simple and the processes are environmentally benevolent (**Keow man *et al*.,2006**)

The scope of microwave radiation for organic bromination reactions are reported (**Alimenla *et al*.,2006**). Results reveal that these radiation-induced reactions are unique in their high yields and that they require extremely short reaction times compared with conventional room-temperature reactions. In these reactions tetrabutyl ammonium tribromide was used as an alternative brominating reagent in order to avoid the chemical hazards associated with liquid bromine. As all the reactions were successfully carried out in solid-state under microwave conditions, the use of solvent was not required. All these aspects make the bromination protocol quite environment friendly.It is very convenient to carry out organic bromination reactions by using microwave radiation. The reactions are very fast compared with reactions performed by conventional methods and a variety of organic brominations reactions can be performed.

2.1.1 Microwave assisted synthesis of heterocyclic compounds

An improved practical method is described for the generation of benzonitrile sulfide based on microwave-assisted decarboxylation of 5-phenyl-1,3,4-oxathiazol-2- one. Reaction times for the preparation of cycloadducts (e.g. isothiazoles and 1,2,4- thiadiazoles) derived from the nitrile sulphide are reduced from typically 15–30h to approximately 15min.It is being clear that the time needed for the reaction moreover less than the conventional synthesis (**Paton *et al.*,2005).**

A novel and efficient method for the synthesis of substituted thieno[2,3-b]quinolines has been developed by (**Nandeshwarappa *et al*.,2005**). Here a simple one-pot reaction of 3-formyl-2-mercaptoquinolines2a–l with 1-chloroacetone, 2-chloroacetamide, ethylchloroacetate and 2-chloro-1-phenylethanone in presence of catalytic amount of potassium carbonate under microwave irradiation and solvent-free conditions gave thieno[2,3- b]quinolin-2-ylethanone derivatives , thieno[2,3-b]quinoline-2-carboxamide derivatives , ethyl thieno[2,3-b]quinoline-2-carboxylate and phenyl(thieno[2,3-b]quinolin-2-yl)methanone derivatives compounds respectively.

Quinolines were readily prepared under new convenient conditions using poly(N,N- dibromo-N,N-dimethylenebenzene-1,3-disulfonamide) (PBBS) or N,N,N,N-tetra bromo benzene-1,3-disulfonamide (TBBDA) as efficient reagents from 2-aminobenzophenones and ketones or phenylacetylene under microwave/solvent-free conditions in good to excellent yields. It has been established that TBBDA and PBBS as efficient reagents for the preparation of quinolines from o-aminoarylketones and different ketones or phenylacetylene under solvent-free/microwave irradiation conditions. This method not only provides an excellent complement to quinoline synthesis, but also avoids the use of hazardous and environmentally unfriendly acids or bases (**Vaghei*et al*.,2010**).

Synthesis of 4-quinolone-3-carboxylic esters and 4-quinolone-3-carbonitriles under microwave activation using anilines and acrylates as materials. All reactions demonstrated the benefits of microwave reactions: convenient operation, short reaction time, and good yields. This work demonstrates an easy and convenient method for synthesizing 4-quinolone-3-carboxylic esters and 4-quinolone-3- carbonitriles under MW irradiation. The solvent-free method for the condensation step proved to be more efficient and friendlier to the environment than the classical procedures because it avoids using organic solvents during the reactions. The MW-assisted cyclization reactions take place at relatively low temperatures and within short times compared to the classical methods. This method also simplifies the handling of the reactions and gets good yields of 4-quinolone derivatives (**Cao *et al*., 2009**).

The direct esterification, thioesterification and amidation of cyclic phosphinic acids, such as 1-hydroxy-3-phospholene 1-oxides, 1-hydroxy-phospholane 1-oxides and a 1-hydroxy- 1,2,3,4,5,6-hexahydrophosphinine 1-oxide, which do not take place on conventional heating, were carried out under microwave conditions in excess of the alcohol, thioalcohol and amine, respectively. The cyclic phosphinates were also prepared by MW-assisted alkylating esterification of the corresponding phosphinic acids in solid–liquid phase. Here it has been reported that microwave irradiation promoted transformations that are otherwise impossible on conventional heating.In other instances, such as Diels–Alder reactions, Michael additions and Kabachnik–Fields condensations, the microwave irradiation allows faster, more selective, and hence more efficient transformations (**Keglevich, 2014**).

Microwave technology aided by solid supports-alumina, montmorillonite clay, bentonite, silica gel , dowex and amberlite has been employed for the synthesis of few 4- substituted-3-vinyl quinolines and 4-substituted-3-vinyl quinoline-2(1H)-thiones (**Lalitha *et al*.,2010**). The results of the microwave reactions aided by solid supports indicate significant increase in the yield of product and reduction in the time of synthesis compared to classic conditions and in microwave reactions without solid supports. Neutral alumina and K10 clay were found to be more efficient in the synthesis of chloro -4- alkyl -3-vinyl quinolines and 4- alkyl -3-vinyl quinoline-2(1H)- thiones.It has been reported that microwave reactions aided by solid supports indicate significant increase in the yield of product and reduction in the time of synthesis compared to classic conditions and in microwave reactions without solid supports.

2.2 *In vitro* DNA binding studies

DNA binding is the critical step for many cytotoxic metal complexes as DNA is the primary intracellular target of antitumor drugs. Coordination compounds offer many binding modes to polynucleotides, including outer-sphere non-covalent binding, metal coordination to nucleobases and phosphate backbone interactions (**Mathur *et al.*,2008**).

2.2.1 *Ct*-DNA binding studies of inorganic complexes

The interaction of copper (II) complex with calf thymus (CT-DNA) has been studied by using absorption, emission and circular dichroic spectral methods, viscometry, and cyclic voltammetry. A strong hyperchromism along with a red shift in UV bands and hypochromism in the ligand field band of the complex on interaction with CT-DNA imply a covalent mode of DNA binding (**Mathur *et al.*,2008**).

N,N' bis(3,4 dihydroxyhenzylidene) 1,2 diaminobenzene (BDBDAB), have been synthesized by combination of 1,2 diaminobenzene and 3,4 dihydroxybenzaldehyde. These ligands containing ortho quinone functional groups were characterized using UV-Visible and IR spectroscopies. Subsequently, the interaction between native calf thymus deoxyribonucleic acid (ct DNA) has been studies and confirmed using UV visible absorption and fluorescence spectroscopies, thermal denaturation technique, viscosity measurement, and cyclic voltammetry. The binding constants of BDBDAB with double stranded DNA were found to be (0.9 ± 0.1) × 10^4 M^{-1}.Results suggest that interaction with the grooves could be the principal mode of binding of BDBDAB to double stranded ct DNA (**Azania*et al*.,2010**).

The interaction of 1,10-phenanthroline octyl dithiocarbamatopalladium (II) nitrate with Ct-DNA is reported. Results of UV-visible studies show that the complex exhibits cooperative binding with DNA and denatures the DNA at an extremely low concentration. Fluorescence studies reveal that the mode of binding of this complex with DNA seems to be intercalation. The results of sephadex G-25 column show that the binding of metal complex with DNA is so strong that it does not readily break. Several binding and thermodynamic parameters are also described (**Torshizi*et al*.,2011**).

The Schiff base ligand, N,N-bis-(2-thiophenecarboxaldimine)-3,3_-diaminobenzidine (L) obtained from condensation of 2-thiophenecarboxaldehyde and 3,3-diaminobenzidine, was used to synthesize the complexes of type, [M2L2]Cl4 [M = Co(II), Ni(II), Cu(II), Cd(II) and Hg(II)]. Absorptionand fluorescence spectroscopic studies evidence Schiff base ligand L and its Co(II), Ni(II) and Cu(II) complexes to show significant binding to calf thymus DNA. The complex interacts with the secondary structure of the calf thymus DNA resulting in its breakage and perturbation The complexes exhibited higher affinity to calf thymus DNA than the free Schiff base ligand L(**Shakir *et al.,*2011**).

For square-pyramidal copper(II) complexes with ciprofloxacin (CFL) in the presence of bipyridine derivatives, the thermal denaturation study has been used for evaluating calf thymus DNA interaction activity. The bathochromicity and hypochromicityobserved in UV–Vis absorption curve for DNA binding experiment is consistent for classical intercalation mode of binding (**Patel*et al*.,2011**).

In copper(II) complexes [Cu(L)(OCN)] and [CuL(dca)]n , where HL = 2-(-(2-(diethylamino) ethylimino)methyl)naphthalen-1-ol, dca = N(CN)2 the interactions of the complexes with calf thymus DNA (CT DNA) were studied by UV–VIS spectroscopy. The first compound has square planar structure and second has square pyramidal structure. It has been revealed that square planar complex was more effective in intercalating DNA than the square pyramidal complex (**Jana et al., 2014**).

Interaction of gold(III) trichlorophenanthridine complex, [Au(phend)Cl3], with calf thymus DNA was investigated by UV–Vis absorption, circular dichroism, and fluorescence spectrophotometery as well as viscometry, cyclic voltammetry (CV), and molecular docking. The values of binding constants Kb (obtained by UV–Vis) and K_f (obtained by fluorescence) are 3×10^4 and 7.68×10^5 M^{-1}. Evidence for intercalation was a hyperchromic effect and a hypochromic effect noted in the spectrum **(Moradi *et al*.,2013).**

2.2.2 Ct-DNA binding studies with organic compounds

The interaction of Ct-DNA with quinolone drugs ciprofloxacin, fleroxacin, gatifloxacin, sparfloxacin with Mg2+ and Cu2+ divalent ions is reported (**Akinremi, 2013**) . In the absence of divalent metal ions, quinolone drugs interact with DNA double helix by forming hydrogen bonds between the carboxyl and carbonyl groups of the drugs and the phosphate groups of the DNA bases, and the binding capacity shows a close relationship with the drug structures. The two metal ions show different influences on the binding between the drug and DNA, which depends on the type of ion, concentration of the metal ions and the structure of drugs. Mg^{2+}act as a bridge between the carboxyl group/carbonyl group of the drug and the phosphate group of the DNA by electrostatic interaction, while Cu^{+2} can act as an intermediary ion between carboxyl group/carbonyl group of the drug and the DNA bases by a co-ordinate bond.

Anthracycline drugs adriamycin and daunorubicin, efficient in the treatment of various human cancers, form strong intercalation complexes with

DNA.1,4-dihydroxy-9,10-anthraquinone (QH_2) is a simple analogue of the anthracyclines also interacts with calf thymus DNA. Intrinsic binding constant is in the order 10^5 mol−1·dm^3 which is greater than those reported for the common anthracyclines (**Guin *et al*., 2011**).

The interaction of 6-methoxyflavanone (6MF, 6-methoxy-2-phenyl-4H-1-benzopyran-4-one) with calf thymus DNA (ctDNA) was investigated by absorption spectroscopy, fluorescence spectroscopy, and cyclic voltammetry in the presence and absence of β-cyclodextrin (β-CD) acting as capping agent.6MF formed a 1 : 1 inclusion complex with β-CD. The binding constant and quenching constant for the interaction of 6MF with ct-DNA are 2.39×10^5 L mol^{-1} and 1.75×10^4 L mol^{-1}. The interaction of 6MF with ctDNA in the presence and absence of β-CD as the capping agent reveals that the dihydrobenzopyran-4-one moiety of 6MF interacts with ctDNA.. The spectral results suggest that the cyclodextrin cavity might not cover the entire dihydrobenzopyran- 4-one moiety from interaction with ctDNA (**Yousuf*et al*.,2012**)

Binding properties of butylated hydroxytoluene (BHT) with calf thymus DNA (ctDNA) by various spectroscopic techniques including UV–Vis absorption, fluorescence and circular dichroism (CD) shows that the binding mode between BHT and ctDNA was an intercalation type. The association constants between BHT and ctDNA were evaluated to be $(4.78 \pm 0.04) \times 10^3$, $(2.86 \pm 0.02) \times 10^3$ and $(1.80 \pm 0.04) \times 10^3$ L mol^{-1} at 298, 304, 310 K respectively. Thermodynamic analysis of the binding data showed that the binding process was primarily driven by hydrogen bonds and van der Waals forces (**Ma*et al*.,2013**).

Metformin and calf thymus DNA (CT-DNA) were studied by UV–Visible absorption, fluorescence, CD spectroscopy and viscosity measurements. In fluorimetric studies, the enthalpy and entropy of the reaction between the drug and CT-DNA showed that the reaction is exothermic. Binding constant, Kb, obtained from UV–Vis absorption studies was 8.3×10^4 M^{-1}. Viscosity measurements revealed that the binding of the complex with CT-DNA could be surface binding, mainly due to groove binding (**Shahabadi*et al*.,2012**).

The binding interaction of tetrabromobisphenol A with Calf thymus DNA was studied by multispectroscopic and molecular modeling methods. The UV–Vis study revealed the interaction between tetrabromobisphenol A and Calf thymus DNA. The π-π*transitions and the electron cloud of tetrabromobisphenol A might be changed by entering the groove of Calf thymus DNA (**Wang*et al*.,2014**).

Interaction of the anticancer plant alkaloid chelerythrine with four sequence specific synthetic polynucleotides was observed by spectroscopy and colorimetry experiments. The binding was in strong hypochromic and bathochromic effects in the absorption spectrum of the alkaloid this shows Chelerythrine binds to these polynucleotides by intercalation (**Basu *et al*.,2014**)

The DNA binding of Aspartame (APM) an artificial sweetener was studied using UV–Visible absorption, fluorescence, CD spectroscopy and viscosity measurements. Hypochromism and red shift are shown in UV absorption band of APM. The binding constant was 5.0 x10^4 M-^{1} which is very less than any other sweetener in food industry. The binding constant indicates that the APM binds with DNA as groove binder. Fluorometric experiments and CD results shows the non-intercalative DNA binding nature of APM (**Kashanian *et al*.,2013**).

2.3 Fabrication of Solar cells using Natural dyes

Extracts from roots of *Beta vulgaris* were used as natural sensitizers of a wide-bandgap semiconductor (CeO_2–TiO_2) in photoelectrochemical solar cells. The natural dye, adsorbed onto the semiconductor surface, absorbs visible light and promotes electron transfer across the dye/semiconductor interface. CeO2–TiO2 applied to natural dye sensitizer solar cells as a photoelectrode reduces the charge recombination rate by providing energy barrier at the interface between the photoanode and electrolyte which offers an improvement of photovoltaic efficiency. Short-circuit current density (Jsc) and open-circuit voltages (Voc) of 9.0 mA cm−2 and 680 mV, respectively, were obtained, and an effective energy conversion efficiency of 3.5% was achieved. This simple and cheap technique of cell preparation opens up a perspective of commercial feasibility for inexpensive and environment-friendly dye cells (**Ruby Upadhyay *et al.,* 2014).**

Natural dyes extracted from the seeds of the achiote shrub (*Bixa orellana* L.) have been used in dye sensitized solar cells(DSCs).The main pigments are bixin and norbixin, which were obtained by separation and purification from the dark-red extract. Solar cells were prepared using TiO_2 and ZnO nanostructured, meso porous films and the annatto, bixin and norbixinas sensitizers. The dyes strongly absorb visible light between 400 and 550 nm and the maximum absorption coefficient of bixin is about 13 times higher than that of the ruthenium-based dye N-719, while the maximum absorption coefficient for norbixin is about the same as for N-719.The best results were obtained with bixin-sensitized TiO2 solar cells with efficiencies of up to 0.53%**(Ortı´z *et al*.,2010).**

The natural dyes extracted from *Hierochloeodorata* (HO), *Toruliniumodoratum* (TO) and *Dactylocteniumaegyptium* (DA) grasses were successfully used as light harvesters in dye sensitized solar cells. The result shows that the maximum efficiency obtained for the cell fabricated with HO grass dye is around 0.46%, whereas the conversion efficiency of the cells fabricated with TO and DA dyes are 0.32% and 0.24% respectively. The high efficiency of DSSC with HO dye is due to the better binding of the dye molecules with TiO_2 layer and huge Charge transfer resistance at TiO2 dye electrolyte interface (**Shanmugam*et al*.,2015**).

Natural dyes as sensitizers of DSCs are promising because of their environmental friendliness, low-cost production, and designable polychrome modules(**Zhou et al.,2011)**. Twenty natural dyes, extracted from natural materials such as flowers, leaves, fruits, traditional Chinese medicines, and beverages, were used as sensitizers to fabricate dye-sensitized solar cells (DSC's). The photoelectrochemical performance of the DSC's based on these dyes showed that the open circuit voltages (Voc) varied from 0.337 to 0.689 V, and the short circuit photocurrent densities (Jsc) ranged from 0.14 to 2.69m Acm^{-2}.

Specifically, a high Voc of 0.686V was obtained from the dye extracted from mangosteen pericarp sensitizer. Begonia, Tangerine peel, Rhododendron, *Fructus lycii*, Marigold ,Perilla, *Herba artemisiae scopariae*, *China loropetal*, Yellow rose, Flowery knotweed, Bauhinia tree, Petunia, Lithospermum, Violet, Chinese rose,Mangosteen pericarp Rose, Lily, Coffee, Broadleaf holly leaf, were the natural dyes used and it was compared with N-719. The dyes extracted from these materials contained cyanine, carotene, chlorophyll, etc.

A dye-sensitized solar cell based on natural betalain pigments from red beet roots and reddish-purple betanin, an easily oxidized, water soluble pigment gives an appreciable efficiency. Photocurrents and photovoltages are also reported for the DSSC sensitized with yellow betaxanthin and brown betalain-derived oxidation products. Though anthocyanins and betalains share a similar biological function, the presence of carboxylic acid functions in the latter presents an advantage for anchoring the dye to the TiO_2 surface by manipulating the surface acid–base chemistry(**Zhang et al,2008**).

Dye-sensitized solar cells (DSSCs) were assembled using red Sicilian orange juice (*Citrus sinensis*) and the purple extract of egg plant peels (*Solanummelongena*, L.) as natural sensitizers of TiO_2 films. Conversion of solar light into electricity was successfully accomplished with both the aforesaid fruit-based solar cells. The best solar energy conversion efficiency (Z ¼ 0.66%) was obtained by red orange juice dye that, under AM 1.5 illumination, achieved up to Jsc ¼ 3.84 mA/cm2, Voc ¼ 0.340 V and fill factor ¼ 0.50.

In the case of the extract of eggplant peels, the values determined were up to Jsc ¼ 3.40 mA/cm2, Voc ¼ 0.350V and fill factor ¼ 0.40. Cyanidine-3-glucoside (cyanine) and delphinidin 3-[4-(p-coumaroyl)-L-rhamnosyl(1–6)-glucopyranoside]-5-glucopyranoside (nasunin) are the main pigments of cocktail dyes for red orange and eggplant, respectively(**Calogero *et al*.,2008).**

The natural dyes carotenoid and anthocyanin were extracted from *Kerriajaponica* and *Rosa chinensis* respectively. The ranges of short-circuit current (JSC) from 0.559 to 0.801 (mA/cm2), open-circuit voltage(VOC) from 0.537 to 0.584 V,and fill factor from 0.676 to 0.705 were obtained for the DSSCs made using the extracted dyes. The efficiencies of the *K. japonica* and *R. chinensis* dyes were 0.22% and 0.29%, respectively; after the addition of sugar, the efficiency increased to 0.29% for *K. japonica* and decreased to 0.27% for *R. chinensis.* Thus, the addition of sugar molecules increased the conversion efficiency slightly with the carotenoid dye of *K.japonica,* while there was no considerable change with the anthocyanin of *R. chinensis* (**Calogero*et al*.,2012).**

2.4 Fabrication of Solar cells using organic dyes

6H-indolo[2,3-b]quinoxaline incorporatedto electron-rich p-conjugated bridges such as oligothiophene, thienyl carbazole, and furyl carbazole have been used in solar cells. Oligothiophene as the p-conjugated linker exhibited a broad region with photocurrent signal up to about 770 nm covering almost the whole visible light range and hence shows best photovoltaic performance and efficiency was found to be 7.62%(**Qian *et al*.,2015**).

Macrocyclic triphenylamine dimer is reported to be a good candidate for dye sensitized solar cells Photovoltaic devices based on these dyes showed high open circuit voltage and achieved a solar energy to electricity conversion efficiency of 6.31%. Macrocyclic triphenylamine acts not only as a secondary electron-donating group, which would retard the rate of charge recombination by increasing the distance between the dye cation center and the TiO_2 surface, but it may be very favorable for the stabilization of the initially formed radical cation since it exhibits good intramolecular electron charge transfer(**Zhao *et al*.,2012**).

10-phenyl-10Hphenothiazine,10-phenyl-10H-phenoxazineand triphenylamine are three dyes which are attached with simple phenoxazine. Four dyes exhibit considerably high values of conversion efficiencies. It can be seen that the structure variation of electron donors have some degree of influence not only on charge combination, but also on conduction-band edge.These four dyes shows efficiencies of 6.6%, 7.8%, 7.1% and 6.4%(**Tan *et al*.,2013**).

2-Cyano-3-*{*5-[2-(1,2,2,4-tetramethyl-1,2,3,4-tetrahydroquinolin-6-yl)-vinyl]-thiophen-2-yl*}*-acrylic acid, 2-Cyano-3-[5-(2-*{*5-[2-(1,2,2,4-tetramethyl-1,2,3,4tetrahydro-quinolin-6-yl)-vinyl]-thiophen-2-yl*}*-vinyl)-thiophen-2-yl]-acrylic acid, 2-Cyano-3-[5-(1,2,2,4-tetramethyl-1,2,3,4-tetrahydro-quinolin-6-yl)-thiophen-2-yl]-acrylic acid these three compounds contains tetrahydroquinoline moiety as the electron donor, different thiophene-containing electron spacers and a cyanoacrylic acid moiety as the electron acceptor. 2-Cyano-3-[5-(1,2,2,4-tetramethyl-1,2,3,4-tetrahydro-quinolin-6-yl)-thiophen-2-yl]-acrylic acid has a rigid electron spacer, has the narrowest action spectrum among these dyes, it gives the highest solar-to-electricity conversion efficiency (*η*) of 4.49%.The work also conclude that largerπ-conjugating systems are expected for better light harvesting ability, and thus better performance of the dyes.(**Chen *et al*.,2007**)

Donor-(π-spacer)-acceptor (D-π-A) organic dyes triphenylamine,di(*p*-tolyl)phenylamine, and 9-octylcarbazole moietiesNanocrystalline TiO2 dye-sensitized solar cells were fabricated by using these dyes. It was found that the variation of electron donors in the D-π-A dyes played an important role in modifying and tuning photophysical properties of organic dyes. Di(*p*-tolyl)phenylamine gives appreciable efficiency and photo current (**DaXi *et al*.,2009**).

2,3-Bis(N-methyl-2′methyl-3′-indolyl)maleic anhydride, 2,3-Bis (N-benzyl-2′methyl-3′-indolyl)maleic anhydride, 2,3-Bis (N-dodecyl-2′methyl-3′-indolyl)maleic anhydride which have indole moiety was used as sensitizers for the application in nanocrystalline TiO_2 solar cells. The indole group,maleimide group and carboxylic group functioned as electron donor, acceptor and anchoring group, respectively. The non-planar structure of bisindolylmaleimide was proven to be effective in aggregation resistance. This work suggests that organic sensitizers with maleimide as electron acceptor are promising candidates as organic sensitizersin dye-sensitized solar cells (**Zhang *et al*.,2009**).

The literature study gives a good guidance to perform the experimental part. On the above mentioned reviews the methodology of the present study has been carried out in two phases.

MATERIALS AND METHODS

3. MATERIALS AND METHODS

The present study entitled "***In vitro* DNA Binding Studies of Selected Heterocyclic Compounds and their Photovoltaic Applications"** was carried out in two phases. The detailed methodology adopted is given below.

The first phase includes the synthesis of some heterocyclic quinolines and DNA binding ability of them. The second phase includes their application in photovoltaic field.

3.1 General

- The chemicals used for the study are of AR grade.
- Highly polymerized ct-DNA, Tris-HCl was purchased from Sigma Co.
- Doubly distilled water was used throughout the experiment.
- $p^H$of the solution was attuned using Eutech p^H metre.
- Microwave reactions were carried out in IFB model 179 MIS of output power 750W and BPL model BMO 800 TS.
- The optical density was measured using Shimadzu Biotech Bio-spec-nano spectrophotometer **(Plate 1**).
- The absorbance of each compound was verified using Systronics 2202 model UV spectrometer **(Plate 2).**
- IR spectra was recorded using Perkin Elmer spectrometer model 599.
- The solar cell was prepared using 1 x 1 cm FTO glass plates.
- The current and voltage was measure using Kusam meco 405 multimeter.
- The light source for the DSSC was a 40V lamp.

Plate 1

Shimadzu Biotech Bio-spec-nano spectrophotometer

Plate 2

Kusam meco 405 multimeter

3.1.1 Purification of solvents

The solvents used for the present study namely ethanol, benzene and hexane were purified by standard procedures (**Vogel,2004**).

3.1.2 Preparation of synthetic compounds

The starting compounds namely 2 amino acetophenone, 2-Aminobenzophenone,2-Amino-5-chlorobenzophenone,2-Amino-5 nitrobenzophenone, vinyl acetic acidwere purchased from Sigma Aldrich

Company. The procedure of **Lalitha *et al*.,2010**was adopted with slight modifications for the preparation of vinly quinolones.

3.2.1 Synthesis of 4-methyl 3-vinyl quinolone-2(1H)-one

2-Aminoacetophenone about 5g was mixed with 2.5g of pyridine in anhydrous benzene of about 120ml.After the solution was cooled about 4.5g of 3-butenoyl chloride dissolved in benzene was added drop wise with shaking. For one hour the reaction mixture is cooled after that it is poured into ice-cold water. The separated benzene layer is removed and further washing with ice-cold dilute hydrochloric acid, aqueous sodium bicarbonate and water, then the solvent was evaporated. The obtained residue was dissolved in 50ml of ethanol and which contains 2.5g of potassium hydroxide. For an hour it was kept aside in room temperature and then it was poured into ice-cold water and the resulting solution was neutralized with dilute hydrochloric acid. The solid which precipitated was collected, washed with water and recrystallized from alcohol. The obtained aqueous layer after the separation of benzene was shaken with 25ml of chloroform. The chloroform layer was washed with dilute HCl, aqueous sodium bicarbonate and finally with water. The residue thus obtained was dissolved in ethanol and poured into ice cold water. The solution was neutralized with dilute HCl to get the final product.

3.2.2 Synthesis of 4-phenyl 3-vinyl quinolone-2(1H)-one

2-Aminobenzophenone about 2g was mixed with 0.9g of pyridine in anhydrous benzene of about 30ml.After the solution was cooled about 1.2g of 3-butenoyl chloride dissolved in benzene was added drop wise with shaking. For one hour the reaction mixture is cooled after that it is poured into ice-cold water. The separated benzene layer is removed and further washing with ice-cold dilute hydrochloric acid, aqueous sodium bicarbonate and water, then the solvent was evaporated. The obtained residue was dissolved in 20ml of ethanol and which contains 0.5g of potassium hydroxide. For an hour it was kept aside in room temperature and then it was poured into ice-cold water and the resulting solution was neutralized with dilute hydrochloric acid. The solid which precipitated was collected, washed with water and recrystallized from alcohol. The obtained aqueous layer after the separation of benzene was shaken with 25ml of chloroform. The chloroform layer was washed with dilute HCl, aqueous sodium bicarbonate and finally with water. The residue thus obtained was dissolved in ethanol and poured into ice cold water. The solution was neutralized with dilute HCl to get the final product.

3.2.3 Synthesis of 6-chloro-4-phenyl 3-vinyl quinolone-2(1H)-one

2-Amino-5-chlorobenzophenone about 2.05g was mixed with 0.7g of pyridine in anhydrous benzene of about 32.5ml.After the solution was cooled about 0.9g of 3-butenoyl chloride dissolved in benzene was added drop wise with shaking. For one hour the reaction mixture is cooled after that it is poured into ice-cold water. The separated benzene layer is removed and further washing with ice-cold dilute hydrochloric acid, aqueous sodium bicarbonate and water, then the solvent was evaporated. The obtained residue was dissolved in 20ml of ethanol and which contains 2g of potassium hydroxide. For an hour it was kept aside in room temperature and then it was poured into ice-cold water and the resulting solution was neutralized with dilute hydrochloric acid. The solid which precipitated was collected, washed with water and recrystallized from alcohol. The obtained aqueous layer after the separation of benzene was shaken with 25ml of chloroform. The chloroform layer was washed with dilute HCl, aqueous sodium bicarbonate and finally with water. The residue thus obtained was dissolved in ethanol and poured into ice cold water. The solution was neutralized with dilute HCl to get the product.

3.2.4 Synthesis of 6-Nitro-4-phenyl 3-vinyl quinolone-2(1H)-one

2-Amino-5-nitrobenzophenone about 1.2g was mixed with 1g of pyridine in anhydrous benzene of about 30ml.After the solution was cooled about 1.05g of 3-butenoyl chloride dissolved in benzene was added drop wise with shaking. For one hour the reaction mixture is cooled after that it is poured into ice-cold water. The separated benzene layer is removed and further washing with ice-cold dilute hydrochloric acid, aqueous sodium bicarbonate and water, then the solvent was evaporated. The obtained residue was dissolved in 15ml of ethanol and which contains 1.5g of potassium hydroxide. For an hour it was kept aside in room temperature and then it was poured into ice-cold water and the resulting solution was neutralized with dilute hydrochloric acid. The solid which precipitated was collected, washed with water and recrystallized from alcohol. The obtained aqueous layer after the separation of benzene was shaken with 25ml of chloroform. The chloroform layer was washed with dilute HCl, aqueous sodium bicarbonate and finally with water. The residue thus obtained was dissolved in ethanol and poured into ice cold water. The solution was neutralized with dilute HCl to get the product.

3.3 Microwave assisted reactions

3.3.1 Microwave synthesis of 2-chloro-4-methyl-3-vinyl quinolines

4-methyl 3-vinyl quinolone-2(1H)-one of about 50mg was microwaved at 350W by adding 0.2ml $POCl_3$ in IFB model 17MIS domestic microwave oven. After the completion of reaction the reaction mixture was cooled and poured into ice cold water. It was then neutralized with ammonia. The mixture was extracted with chloroform and chloroform extract was washed with water and dried and evaporated. The residue obtained was column chromatographed over alumina and eluted with benzene-pet ether mixture.

3.3.2 Microwave synthesis of 2-chloro-4-phenyl-3-vinyl quinolines

4-phenyl 3-vinyl quinolone-2(1H)-one of about 50mg was microwaved at 350W by adding 0.1ml $POCl_3$ in IFB model 17MIS domestic microwave oven. After the completion of reaction the reaction mixture was cooled and poured into ice cold water. It was then neutralized with ammonia. The mixture was extracted with chloroform and chloroform extract was washed with water and dried and evaporated. The residue obtained was column chromatographed over alumina and eluted with benzene-pet ether mixture.

3.3.3 Microwave synthesis of 2,6-Dichloro-4-phenyl-3-vinyl quinolines

6-chloro-4-phenyl 3-vinyl quinolone-2(1H)-one of about 50mg was microwaved at 350W by adding 0.1ml $POCl_3$ in IFB model 17MIS domestic microwave oven. After the completion of reaction the reaction mixture was cooled and poured into ice cold water. It was then neutralized with ammonia. The mixture was extracted with chloroform and chloroform extract was washed with water and dried and evaporated. The residue obtained was column chromatographed over alumina and eluted with benzene-pet ether mixture.

3.3.4 Microwave synthesis of 6-nitro-2-chloro-4-phenyl-3-vinyl quinolines

4-methyl 3-vinyl quinolone-2(1H)-one of about 50mg was microwaved at 350W by adding 0.2ml $POCl_3$ in IFB model 17MIS domestic microwave oven. After the completion of reaction the reaction mixture was cooled and poured into ice cold water. It was then neutralized with ammonia. The mixture was extracted with chloroform and chloroform extract was washed with water and dried and evaporated. The residue obtained was column chromatographed over alumina and eluted with benzene-pet ether mixture.

3.3.5 Microwave synthesis of 4-methyl-3-vinyl quinoline-2(1H)-thiones

2-chloro-4-methyl-3-vinyl quinolines about 50mg(0.005mole), thiourea about 25mg(0.007 mole) and 0.25ml anhydrous ethanol was microwaved at 750W in a microwave oven. After the completion of reaction the mixture was cooled, poured into ice water and the obtained yellow solid was collected. The yellow solid is thiouronium salt is washed with ethanol and then digested with 10% aqueous NaOH on steam bath for 30min.Thione as a yellow powder is recovered from alkaline extract by acidification. From the alcoholic filtrate was treated with 10% aqueous NaOH on steam bath for 30min and acidified after cooling. The product was collected and dried and purified.

3.3.6 Microwave synthesis of 4-phenyl-3-vinyl quinoline-2(1H)-thiones

2-chloro-4-phenyl-3-vinyl quinolines about 60.5mg(0.005mole), thiourea about 26.5mg(0.007 mole) and 0.25ml anhydrous ethanol was microwaved at 750W.After the completion of reaction the mixture was cooled, poured into ice water and the obtained yellow solid was collected. The yellow solid is thiouronium salt is washed with ethanol and then digested with 10% aqueous NaOH on steam bath for 30min.Thione as a yellow powder is recovered from alkaline extract by acidification. From the alcoholic filtrate was treated with 10% aqueous NaOH on steam bath for 30min and acidified after cooling. The product was collected and dried and purified. 0.25ml.

3.3.7 Microwave synthesis of 6-Nitro-4-phenyl-3-vinyl quinoline-2(1H)-thiones

6-nitro-2-chloro-4-phenyl-3-vinyl quinolines about 55mg(0.005mole), thiourea about 28mg(0.007 mole) and 0.25ml anhydrous ethanol was microwaved at 750W.After the completion of reaction the mixture was cooled, poured into ice water and the obtained yellow solid was collected. The yellow solid is thiouronium salt is washed with ethanol and then digested with 10% aqueous NaOH on steam bath for 30min.Thione as a yellow powder is recovered from alkaline extract by acidification. From the alcoholic filtrate was treated with 10% aqueous NaOH on steam bath for 30min and acidified after cooling. The product was collected and dried and purified.

3.3.8 Microwave synthesis of 2, 3-dihydro-4-methyl-thieno(2,3-b) quinoline

4-methyl-3-vinyl quinoline-2(1H)-thiones about 60mg was irradiated under microwave at 300W with sodium acetate 50mg and glacial acetic acid 5 drops. The product was obtained within 25seconds. The reaction was further continued for one minute. After the completion of reaction mixture was cooled, poured into ice cold water and extracted with chloroform. The extract was dried. The dried extract gives a residue which is chromatographed over alumina in benzene gave dihydrothieno quinoline which is a colourless needle.

3.3.9 Conversion of 4-methyl-3-vinyl quinoline-2(1H)-thiones to 2,2’-(4,4-dimethyl-3,3’-divinyl)disulphide

4-methyl-3-vinyl quinoline-2(1H)-thiones about 50mg was heated with 15ml of chloroform and 2.5mg $CaCl_2$ on a steam bath for 20min. When reaction proceeds the yellow solution turns reddish brown. After the completion of reaction the reaction mixture was poured into water the residue which is red powder was filtered off to yield crude product. The product obtained is a dimer which is chromatographed over a column of alumina by eluting benzene-pet ether mixture.

For convenience acronyms are assigned to the synthetic compounds and hitherto these acronyms will be used in the thesis :

Table 1: List of acronyms used for the compounds

S.No	IUPAC Names	Acronyms used
1	2-Aminoacetophenone	2-AAP
2	4-methyl 3-vinyl quinolone-2(1H)-one	4MVQ
3	2-chloro-4-methyl-3-vinyl quinolines	2CMVQ
4	4-methyl-3-vinylquinoline-2(1H) thiones	4MVQT
5	2, 3-dihydro-4-methyl-thieno(2,3-b) quinoline	DMTQ
6	4-methyl-3-vinyl quinoline-2(1H)-thiones to 2,2'-(4,4-dimethyl-3,3'-divinyl)disulphide	DDDS
7	2-Aminobenzophenone	ABP
8	4-phenyl 3-vinyl quinoline-2(1H)-one	4PVQ
9	2-chloro-4-phenyl-3-vinyl quinoline	2CPVQ
10	4-phenyl-3-vinylquinoline-2(1H)-thiones	4PVQT
11	2-Amino-5-chlorobenzophenone	ACBP
12	6-chloro-4-phenyl 3-vinyl quinolone-2(1H)-one	6CPVQ
13	2,6-Dichloro-4-phenyl-3-vinyl quinoline	DCPVQ
14	2-Amino-5-nitrobenzophenone	ANBP
15	6-Nitro-4-phenyl 3-vinyl quinoline-2(1H)-one	6NPVQ
16	6-nitro-2-chloro-4-phenyl-3-vinyl quinoline	6NCPVQ
17	6-Nitro-4-phenyl-3-vinyl quinoline-2(1H)-thiones	6NPVQT

3.4 *Invitro* DNA binding studies

Double distilled water was used throughout the study. The chemicals used were purchased from Sigma Co.

3.4.1 Preparation of Tris-HCl buffer

Tris-HCl (10mM-10ml solution) was prepared from 0.1576g Tris-(hydroxymethyl)-amino-methane-hydrogen chloride in 10ml of water. The P^H was adjusted to 7.4.

3.4.2 Preparation of DNA stock solution

The CT-DNA was dissolved in 10mM Tris HCl buffer at P^H 7.4.It was dialyzed against the same buffer.

3.4.3 Preparation of stock solution of the heterocyclic compounds

The stock solution of concentration 1×10^{-3} M for all the compounds was prepared by dissolving compounds in distilled ethanol. From the stock solution the further dilution was made and other concentration of 9.09×10^{-4} M and 1.98×10^{-3} M was prepared .

3.5 UV absorption studies

The UV absorption spectra was recorded using SHIMADZU BIOTECH (Bio-spec-Nano spectrophotometer). The study was conducted by keeping the concentration of ct-DNA constant and varying the concentration of the organic compounds. The three different concentration of organic compound was prepared such as 1×10^{-3} M, 9.09×10^{-4} M and 1.98×10^{-3} M 5µL of ct-DNA and 5µL of the 3 different concentration of organic compounds was taken in tubes and compounds were allowed to interact with ct-DNA. After 1hr optical density measurement was recorded. This was done upto 4hrs.

3.6 Preparation of DSSC

The solar cells were fabricated according to the following procedure with slight modifications **(Kelvin *et al*., 2012).**

3.6.1 Coating the Glass Plates

Two equal-sized FTO glass plates of length and breadth 1 x 1 cm were taken. The plates were handled only at the edges. The plate faces were tested for conductivity by touching the surfaces with the leads from a multimeter. Once the conductive side of the plate was established, the plates were placed side by side in such a way that for one plate the conductive side was up and for the other plate the conductive side down.

A transparent tape was applied to the plates to hold the plates in place for the next step. The tape was placed along either of the long side of the plates to overlap 1 millimeter of the edges.The tape was also placed over the outer of the conductive side up plate. Tin oxide and Titanium dioxide mixture was ground for 30 minutes and coated on to the glass plates. Dried the glass plate in hot plate for 30 minutes. The conductivity was then checked using a multimeter. The organic compounds were sprayed onto the titanium coated plate. After coating the conductivity was again checked.

Another plate was tested to find its conductive side. The side that doesn't conduct was marked with a plus sign (+). A thin carbon coating was applied to the conductive side of the cleaned plate uniformly.

3.6.2 Assembling the Solar Cell

The carbon-coated plate was placed on the titanium-dioxide plate with the coatings touching in such a manner so that the plates are slightly offset. Binder clips were used on the long edges to hold them in place. Drops of an iodide solution is applied to the exposed coating and allowed the solution to soak through the plate coatings so they're covered completely. The iodide solution will enable electrons to flow from the titanium-dioxide-coated plate to the carbon-coated plate when the cell is exposed to a light source thus serving the role of an electrolyte. Excess solution is wiped off from the exposed portions of the plates**.**

3.6.3Activating and Testing the Solar Cell

- An alligator clip was attached to the exposed coated sections on either side of the solar cell.
- The black wire of the multimeter was then connected to the clip which was connected to the exposed titanium dioxide coating. This plate serves as the solar cell's negative electrode, or cathode.
- The red wire of the multimeter was connected to the clip connected to the exposed carbon coating. This plate serves as the solar cell's positive electrode, or anode.
- The solar cell is exposed to a light source with the negative electrode facing the source.

- The current and voltage generated by the solar cell is measured with the multimeter. This procedure is repeated before and after exposed to the light source.

RESULTS AND DISCUSSION

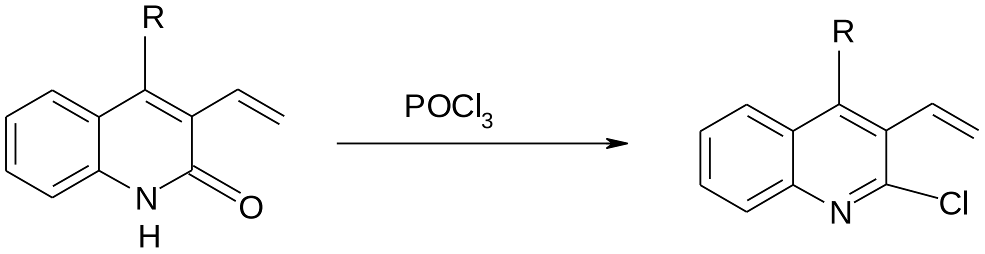
4. Results and Discussion

The results and discussion on the extant study entitled "***In vitro* DNA Binding Studies of Selected Heterocyclic Compounds and their Photovoltaic Applications**" is deliberated in the following folios.

4.1 Microwave assisted synthesis of heterocyclic compounds

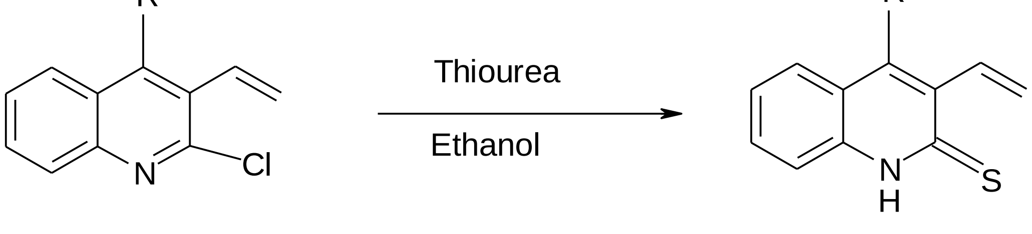
Microwave method of synthesis offers a bundle of advantages. This is exemplified by the increasing number of research work in this field. The major drawback in the conventional means of heating reaction mixture is that the highest temperature that can be achieved is limited by the boiling point of the mixture. This particular type of problem can be avoided by the microwave heating (**Lalitha *et al*.,2007**). In the present study the scheme followed for the microwave synthesis is shown in **scheme A**.

Synthesis of 4-alkyl-2-chloro-3-vinyl quinolines from 4-alkyl-3-vinyl quinolines-2(1H)-one



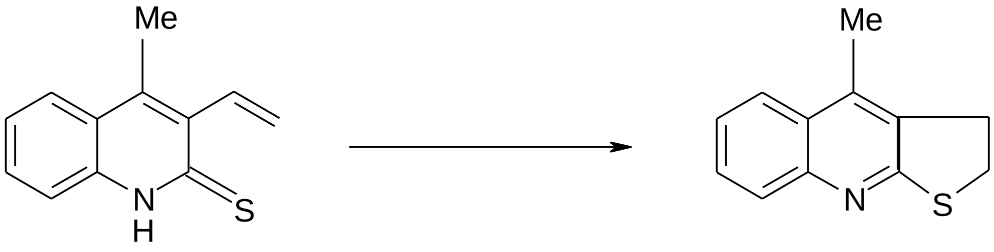
(R=CH_3, C_6H_5, Cl, NO_2)

Conversion of 4-alkyl-2-Chloro-3-vinyl quinolines to the corresponding 3-vinyl quinolines-2(1H)-thione

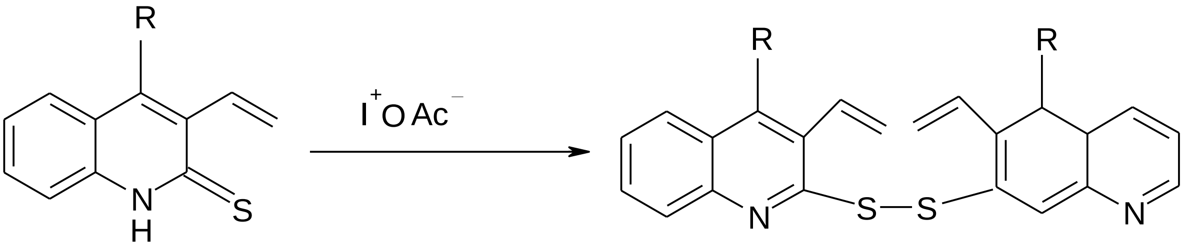


(R=CH_3, C_6H_5, NO_2)

Conversion of 3-vinyl quinoline-2(1H)-thione to 2,3-dihydro-4-methylthieno(2,3-b)quinoline



Conversion of 3-vinyl quinoline-2(1H)-thione to the corresponding disulphides



(R= CH_3)

Scheme A

The yields obtained for the reaction and the time for each reaction to complete are appreciable. In conventional methods of synthesis of these compounds takes about 2-5 hours where as in microwave method the product is obtained in few minutes. The yield of compounds in conventional synthesis was low compared to microwave synthesis(**Table2**). Microwaves cause rapid dispersion of particles and cause the reactants to mix and react at a faster rate enabling quick product formation.

Table 2.Yields of compounds and time of reaction in microwave enhanced synthesis

S.No.	Sample	Yield (%)	Time(min)
1	2CMVQ	90.0	21/2
2	4MVQT	88.0	3
3	DMTQ	83	10
4	2CPVQ	90.4	61/2
5	4PVQT	86.8	4-5
6	DCPVQ	94.3	6
7	6NCPVQ	84.3	9
8	6NPVQT	88.0	8

From the yields and time for the product formation it is evident that microwave assisted synthesis of the heterocyclics is a convenient method of synthesis.

4.2 Characterization of compounds

The sythesized compounds were characterized using UV-visible spectroscopy and IR spectroscopy. The spectra and spectral results are shown below. The TLC of synthesized compounds were matched with authentic samples and confirmed to the same. Also since the IR finger print of the compounds, the region where no two compounds have the same IR peak patterns, matched with the authentic samples, characterization of the compounds by other techniques like NMR, mass etc was not attempted

4.2.1 UV-visible absorption of Synthetic compounds

The synthetic heterocyclic compounds and the corresponding starting compounds were characterized using the basic UV-Visible spectroscopic technique.

UV -visible spectroscopy offers information about the chromophoric groups present in a compound. A wide range of information can be obtained from UV spectrum.

Figures 1 to 18 shows the UV-visible spectrum of synthesized compounds. The UV spectrum of **2-aminoacetophenone (Figure 1)** shows absorption at 293nm and 368nm.The two bands corresponds to C=O chromophore.

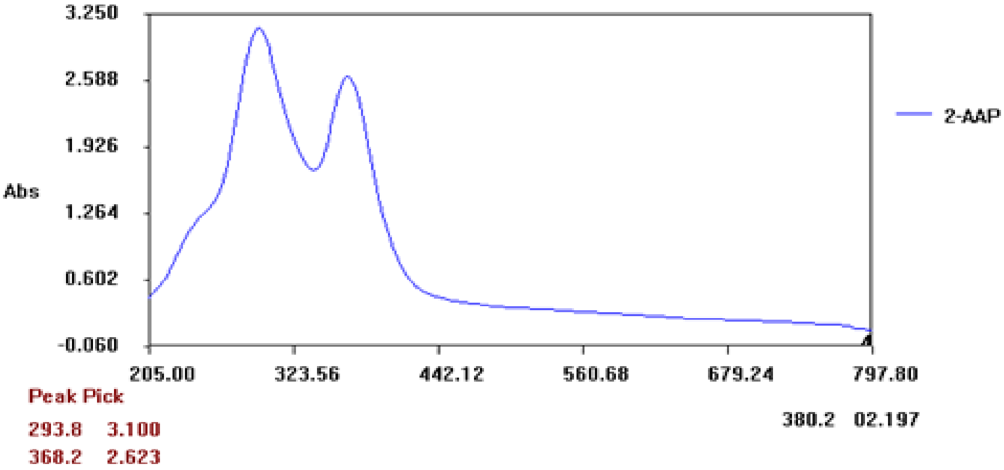


Figure 1. UV-visible spectra of 2-Aminoacetophenone

The UV spectrum of 4-methyl 3-vinyl quinoline-2(1H)-one (**Figure2**) gives absorption bands in the region 258nm to 355nm. This compound gives a broad band.Hence this compound is anticipated to find application in the fabrication of solar cells.

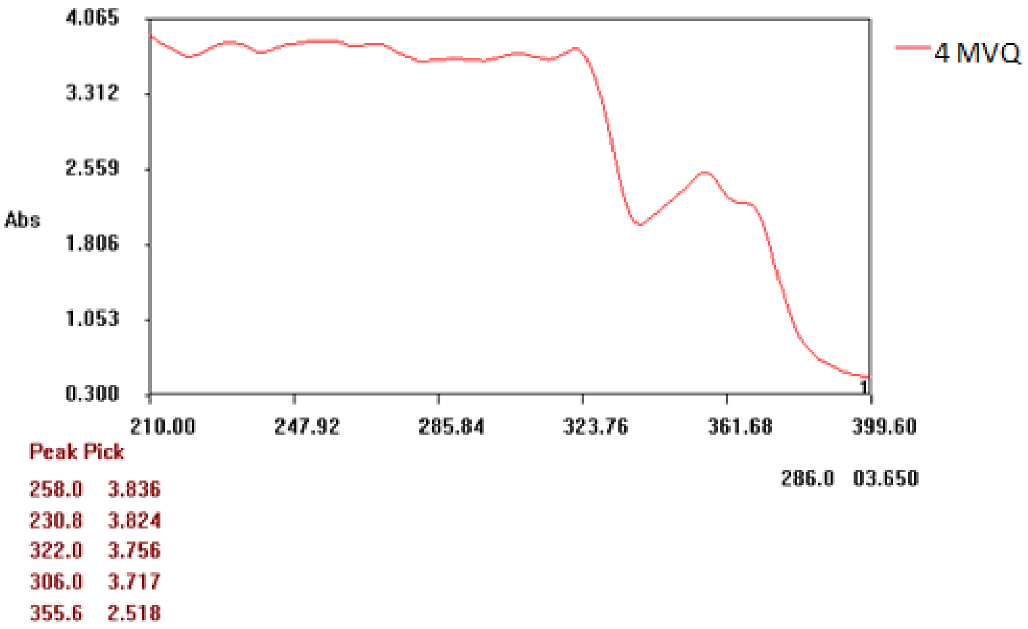


Figure 2. UV-Visible spectrum of 4-methyl 3-vinyl quinoline-2(1H)-one

The absorption spectrum of **2-chloro-4-methyl-3-vinyl quinolines(figure 3)**shows two bands at 260nm and 303nm.The band corresponds to carbonyl and C-Cl chromophore.

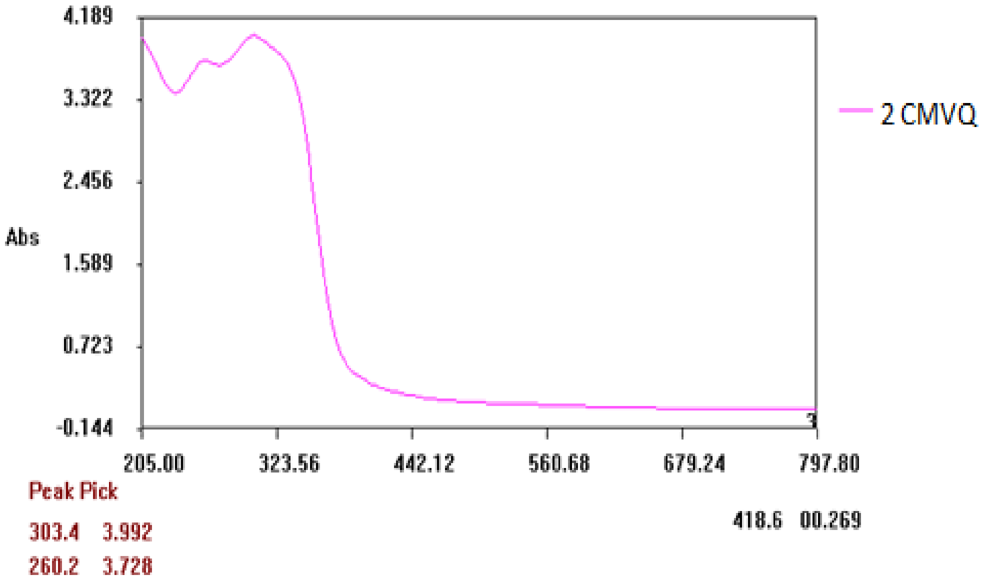


Figure 3: UV-visible spectrum of 2-chloro-4-methyl-3-vinyl quinolines

The λ_{max} for 4MVQT and DMTQ (**Figure 4, Figure 5**) are 298nm, 243nm, 257nm, 317nm.

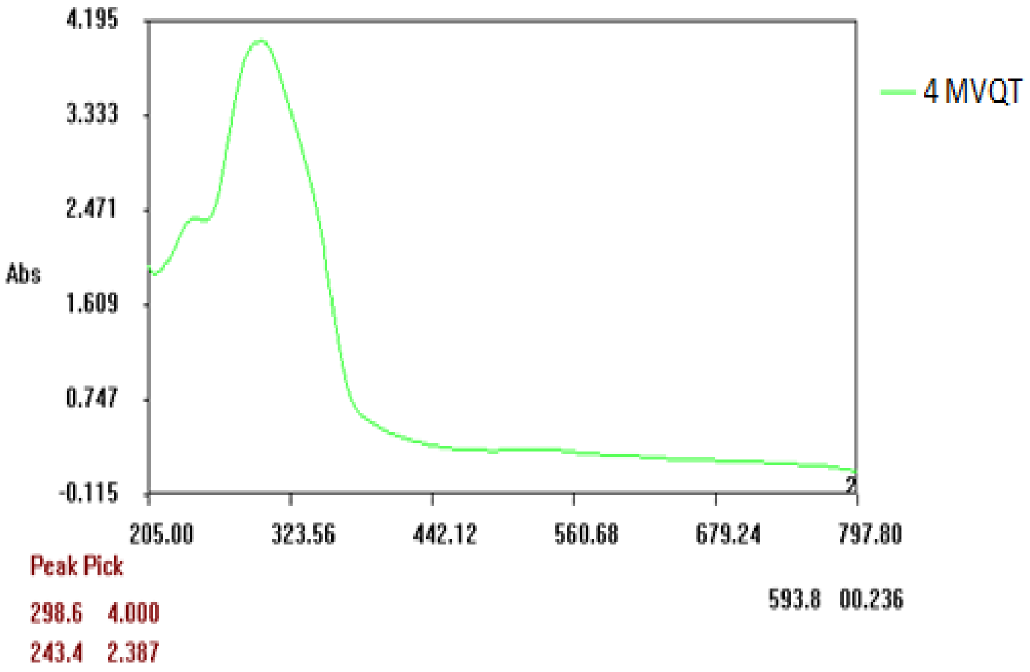


Figure 4.UV-visible spectrum of 4-methyl-3-vinylquinoline-2(1H) thiones

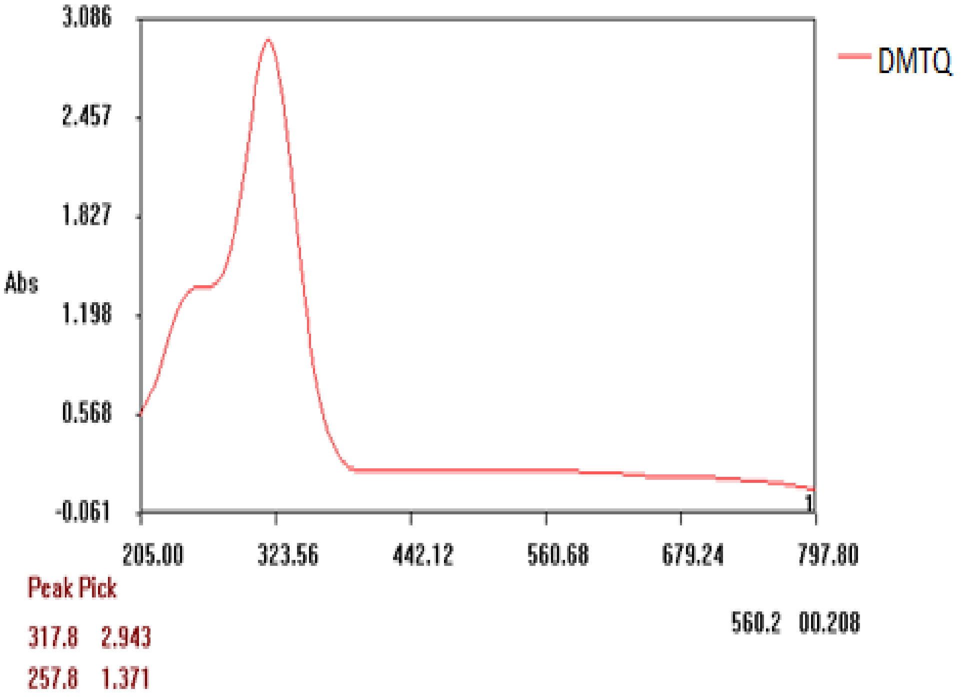


Figure 5.UV-visible spectrum of 2, 3-dihydro-4-methyl-thieno(2,3-b) quinoline

A broad band was obtained for DDDS (**Figure6**) at showing the presence of -C=S chromophoric group. 4PVQ has got only one absorption band 286nm which corresponds to C=O absorption (**Figure 8).**

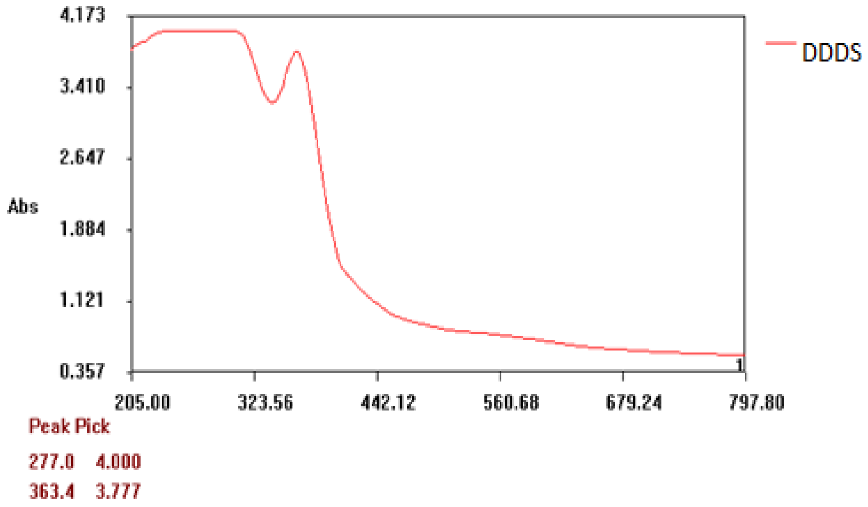


Figure 6. UV-Visible spectrum of 4-methyl-3-vinyl quinoline-2(1H)-thiones to 2,2’-(4,4-dimethyl-3,3’-divinyl)disulphide

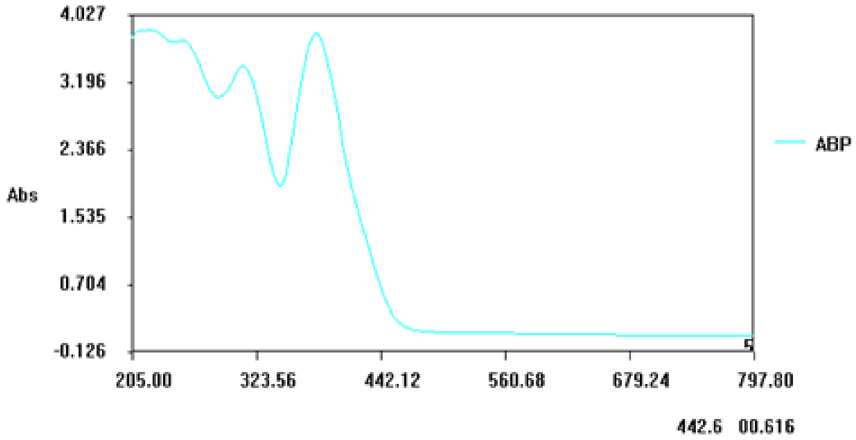


Figure 7. UV-visible spectrum of 2-Aminobenzophenone

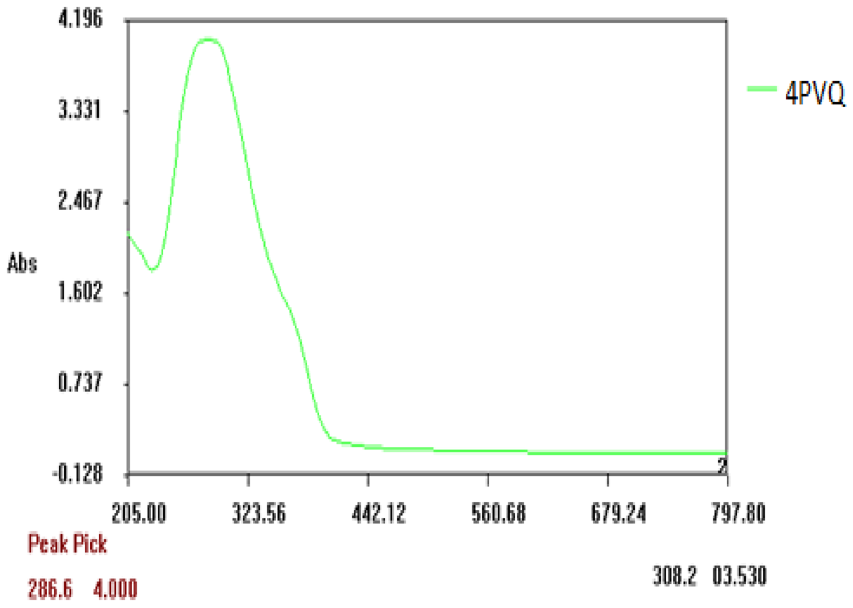


Figure 8.UV-visible spectrum of 4-phenyl 3-vinyl quinoline-2(1H)-one

2CPVQ, 4PVQT have absorption at 229nm and 317nm,which corresponds to C=O absorption.

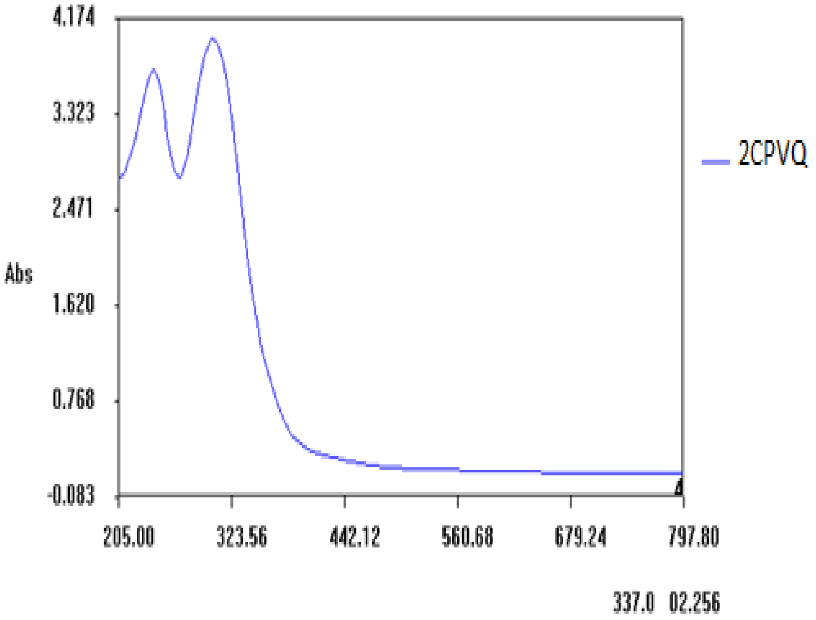


Figure 9. UV-visible spectrum of 2-chloro-4-phenyl-3-vinyl quinoline

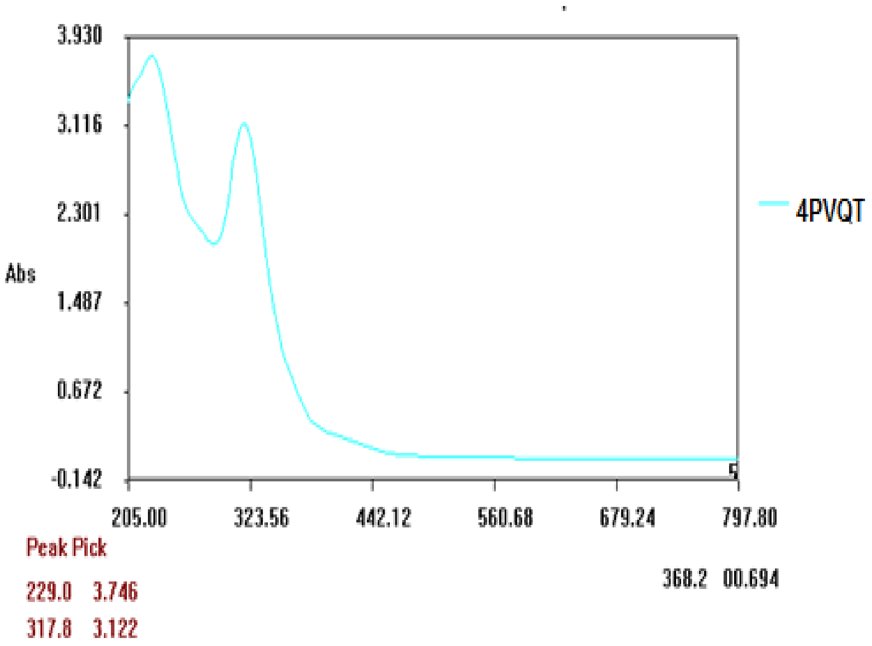


Figure 10.UV-visible spectrum of 4-phenyl-3-vinylquinoline-2(1H)-thiones

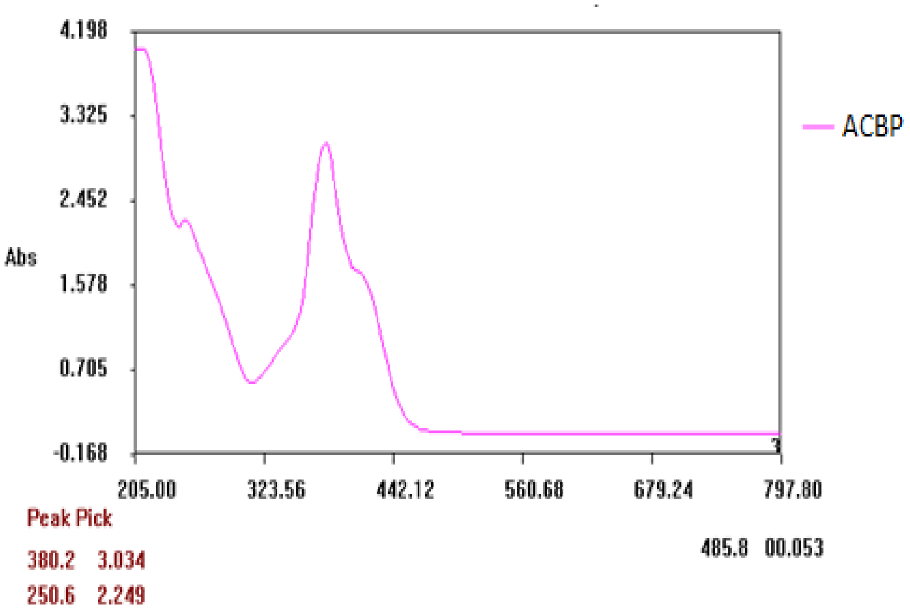


Figure 11. UV-visible spectrum of 2-Amino-5-chlorobenzophenone

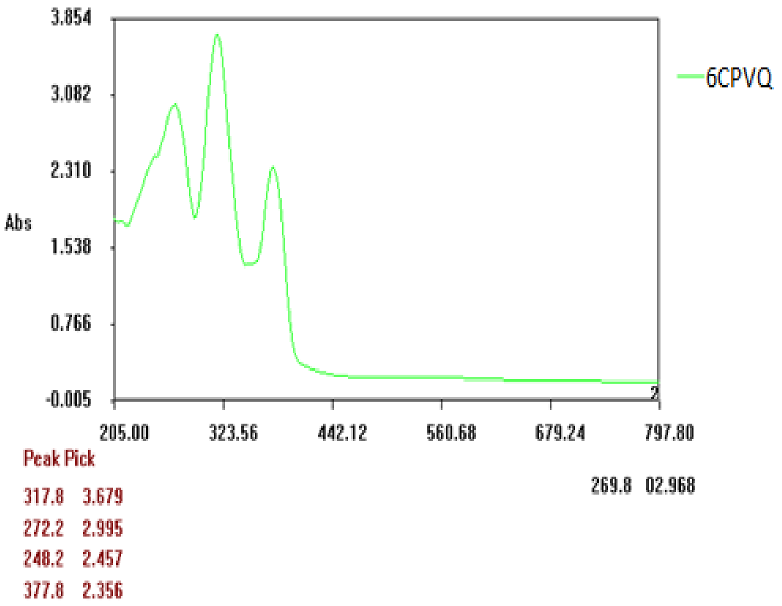


Figure 12. UV-visible spectrum of 6-chloro-4-phenyl 3-vinyl quinolone-2(1H)-one

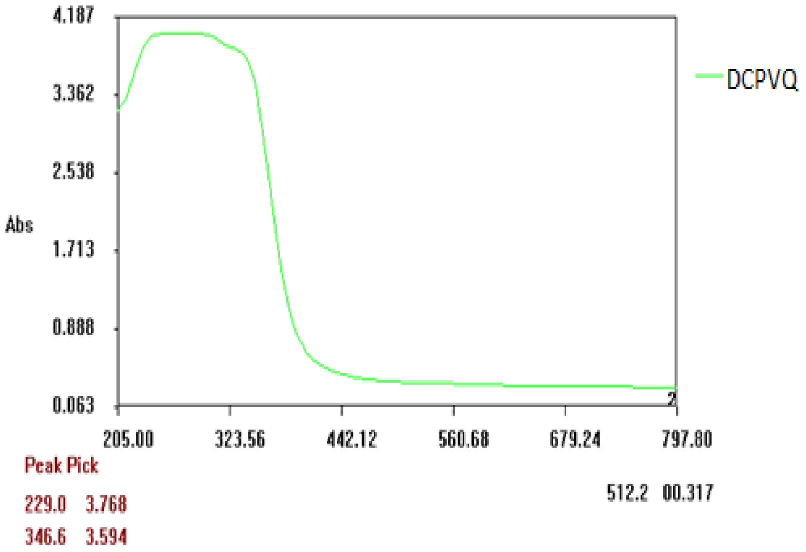


Figure 13. UV-Visible spectrum of 2,6-Dichloro-4-phenyl-3-vinyl quinoline

The absorption of the ANBP ranges from 257nm to 380nm. The substituted derivatives of this compound shows less absorption ranging from 255nm to 365nm (**Figure 14,15,16)**. Compound 6NPVQT has absorption band corresponding to carbonyl and nitro group.

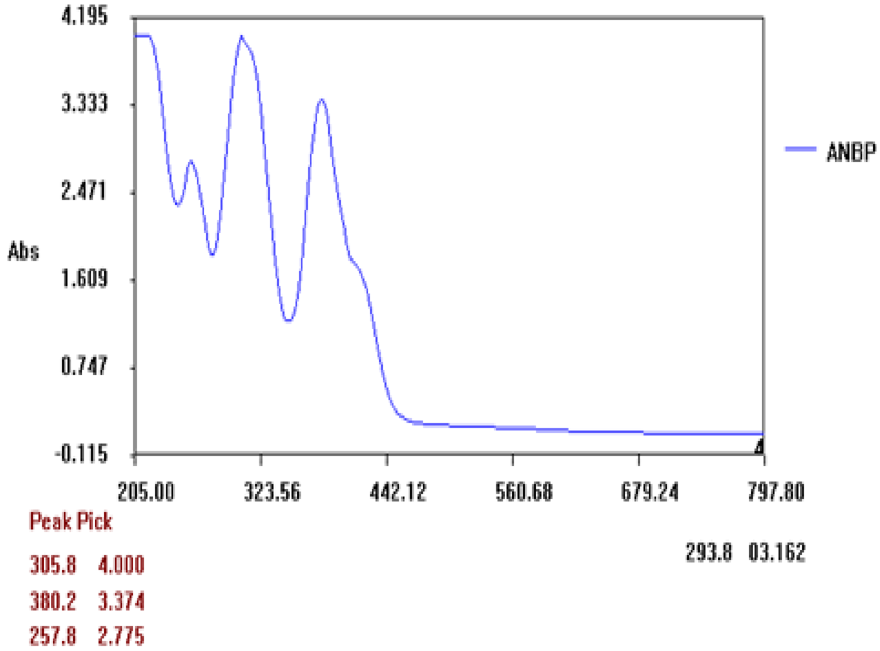


Figure 14.UV-visible spectrum of 2-Amino-5-nitrobenzophenone

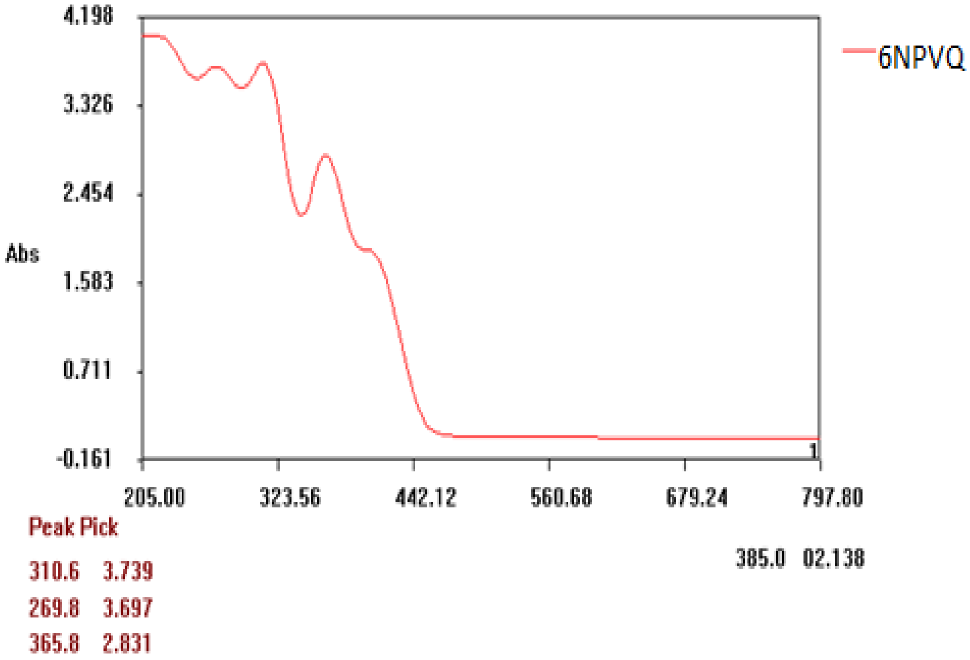
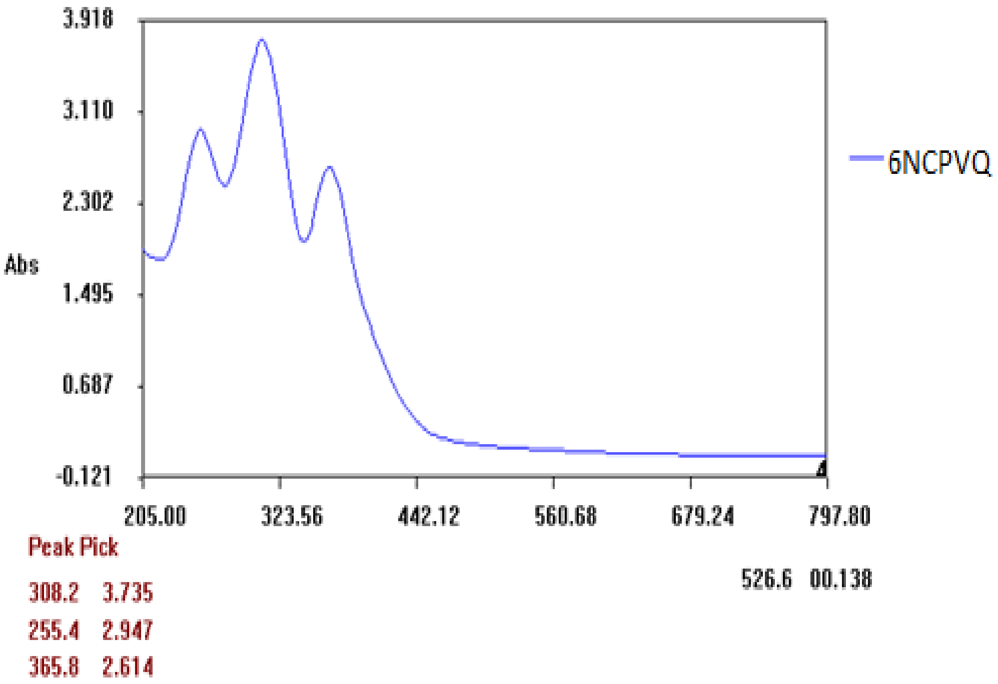


Figure 15.UV-visible spectrum of 6-Nitro-4-phenyl 3-vinyl quinoline-2(1H)-one

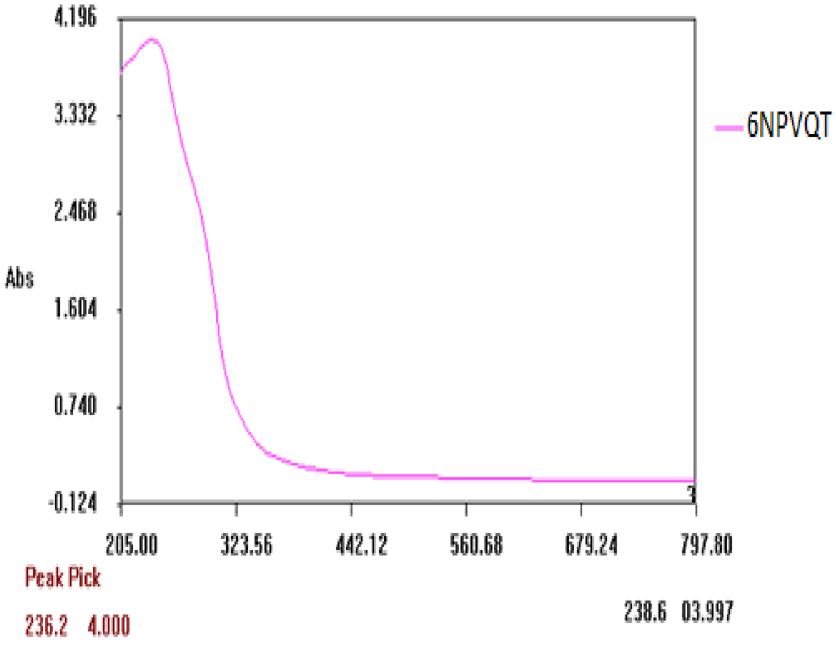


Peak Pick

308.2 3.735
255.4 2.947
365.8 2.614

526.6 00.138

Figure 16.UV-visible spectrum of 6-nitro-2-chloro-4-phenyl-3-vinyl quinoline



Peak Pick

236.2 4.000

238.6 03.997

Figure 17. UV-visible spectrum of 6-Nitro-4-phenyl-3-vinyl quinoline-2(1H)-thiones

4.2.2 FTIR analysis

The FTIR ʋ max in (cm^{-1}) values corresponding to vinyl absorption and thio carbonyl absorption in the finger print region of the synthesized compounds matched with that of standard authentic compounds (**Table 2**) .

Table 3.IR spectral values

Sample	**Spectral values** v **max(cm^{-1})**
4MVQ	1625,935,920(vinyl)
2CMVQ	1620,1550,990,920(Vinyl)
4MVQT	1180 thiocarbonyl,990,935-(Vinyl)
DMTQ	1585
DDDS	1615,1549,980,920(vinyl)
4PVQ	1620,930,910(vinyl)
2CPVQ	1540,990,935(Vinyl)
4PVQT	1190 cm^{-1} due to thio carbonyl absorption 985 and 930 cm^{-1}(vinyl)
6CPVQ	1180,1030,925(vinyl)
DCPVQ	1610,1560,(thio carbonyl) 1030,940(vinyl)
6NPVQ	1650,1020 and 940(vinyl)
6NCPVQ	1640,1580(due to thio carbonyl absorption);1050,945(vinyl)
6NPVQT	1190,1050,945-(Vinyl)

Since there was 100% match of IR spectra in the finger print region, a region where no two compounds will have the same spectral values. other characterization techniques were not adopted .

4.3 DNA binding studies

UV absorption studies were carried out to understand the binding mode of the synthesized compounds to the Ct-DNA. This is one of the preliminary methods and simple spectral technique to understand the binding nature of the compound to DNA. The changes in the absorption pattern help us to study the interaction of DNA with molecules and also its stability.

4.3.1. Quantitation and evaluation of purity of DNA

Quantitation of DNA is commonly carried out to determine the average concentrations of DNA present in a mixture, as well as to determine their purity. Spectrophotometric analysis is one such reliable and economic method is evaluating the purity of DNA. The UV spectrum of DNA is recorded at wavelengths 260nm and 280nm and their optical densities are also recorded. The absorption spectrum of DNA is unique and has a specific pattern. The more the light absorbed by the sample, the higher the DNA concentration in the sample.

The amount of light and the concentration of DNA are correlated by applying Beer's Lamberts law. At 260 nm, the average extinction coefficient for double-stranded DNA is 0.020 $(\mu g/ml)^{-1}$ cm^{-1} and for single-stranded DNA it is 0.027 $(\mu g/ml)^{-1}$ cm^{-1}. An Absorbance of 1 corresponds to a concentration of 50 µg/ml for double-stranded DNA. This method of calculation is valid for up to an absorbance of at least 2 (**Sambrook and Russell, 2001**). A common problem noted in the storing of DNA is its contamination with other molecules. Hence it is very essential to determine the purity of the DNA before studying its interaction with organic molecules of interest. The purity is ascertained by recording the absorbance at 260 and 280 nm (A260/280). For pure DNA, A260/280 is ~1.8.

UV-Vis spectrophotometric optical density (OD) is the most commonly-used technique for estimating chromophore formation and cell concentration in liquid culture. OD wavelength is often chosen with little thought given to its effect on the quality of the measurement. The optical density value provides the relation of absorption at two wavelengths (**John A Myers**, **2013**).In the present study OD value 1.9 was obtained for DNA for A260/280. For studying the interaction of DNA with molecules the absorbance in terms of optical densities is measured.

Quinolines are considered as the DNA intercalators (**Sirajuddin et al.,2013**). There are several work with DNA binding of metal complexes (**Mathur *et al.*,2008, Moradi *et al*.,2013)**. The literature review reveals sparse work with organic compounds and DNA interaction studies. Hence our interest in this area of research.

Here our area of interest is focused on four 4-methyl vinyl quinolone compounds and their derivatives. The results obtained for binding of 2-AAP and their derivatives with DNA revealed its interaction with DNA as evidenced from the shift in the absorption bands. The interaction of DNA with compounds was noted for four different time intervals (**Table 4**). The methyl group along with chloro group, thione ,vinyl quinolines are considered here. They show a decrease in OD value as time increases and the concentration decreases. This was seen in the case of both dihydro and disulphide compounds also. The cause for the difference in OD values for sample with DNA and without DNA are due to the interaction of DNA with the samples. The chloro, nitro groups and olefinic pi electron cloud of these compounds interact with hydrogen bonds in the nucleic acid there by causing a shift from 1.9, the ration of OD at 260/280 which denotes the purity of DNA.

Generally, hypochromic (or hyperchromic) effect and red shift (or blue) shift are observed in the absorption spectra of small molecules if they intercalate with DNA. It is clear from the absorption peaks that there is a bathochromic shift portraying the non-covalent mode of binding to DNA. This type of compounds belongs to the class of DNA intercalators. The bathochromism is because of the decrease in energy between the HOMO and LUMO after the interaction of sample with DNA.As a representatives graphs of this class of compounds the OD vs wavelength plot obtained for these compounds are shown in (**figures 18,19,20 and 21).**

Table 4. Absorbance of samples in terms of optical density for 2-AAP and its derivatives

S.No	Sample	OD 260/280
1	2-AAP (1×10^{-3} M)	-4.35
2	2-AAP (9.09×10^{-4} M)	-2.38
3	2-AAP (1.98×10^{-4} M)	-7.35
4	4MVQ (1×10^{-3} M)	-0.63
5	4MVQ (9.09×10^{-4} M)	-0.24
6	4MVQ (1.98×10^{-4} M)	12.92
7	2CMVQ (1×10^{-3} M)	0.84
8	2CMVQ (9.09×10^{-4} M)	0.71
9	2CMVQ (1.98×10^{-4} M)	2.21
10	4MVQT (1×10^{-3} M)	7.36
11	4MVQT (9.09×10^{-4} M)	14.11
12	4MVQT (1.98×10^{-4} M)	-13.61
13	DMTQ (1×10^{-3} M)	45.97
14	DMTQ (9.09×10^{-4} M)	-26.38
15	DMTQ (1.98×10^{-4} M)	-8.62
16	DDDS (1×10^{-3} M)	6.53
17	DDDS (9.09×10^{-4} M)	18.08
18	DDDS (1.98×10^{-4} M)	-0.76

Table 5. Ratio of optical density values at 260 and 280nm obtained for the AAP and its derivatives with Ct-DNA interaction

S.No.	Sample	OD 260/280			
		1hr	**2hr**	**3hr**	**4hr**
1	2-AAP (1 x 10^{-3} M) +Ct-DNA	**-5.90**	**-7.07**	**-6.68**	**-6.17**
2	2-AAP (9.09 x 10^{-4} M) + Ct-DNA	**5.01**	**4.53**	**5.46**	**9.59**
3	2-AAP (1.98 x 10^{-4} M) + Ct-DNA	**2.00**	**1.82**	**2.04**	**3.51**
4	4MVQ (1 x 10^{-3} M) +Ct-DNA	**-0.42**	**-0.36**	**-0.38**	**-0.26**
5	4MVQ (9.09 x 10^{-4} M) + Ct-DNA	**1.30**	**2.18**	**1.48**	**1.32**
6	4MVQ (1.98 x 10^{-4} M) + Ct-DNA	**1.11**	**1.78**	**1.43**	**1.52**
7	2CMVQ (1 x 10^{-3} M) + Ct-DNA	**1.79**	**1.35**	**1.09**	**1.47**
8	2CMVQ (9.09 x 10^{-4} M) + Ct-DNA	**2.00**	**1.75**	**1.66**	**1.79**
9	2CMVQ (1.98 x 10^{-4} M) + Ct-DNA	**2.52**	**1.43**	**2.00**	**2.02**
10	4MVQT (1 x 10^{-3} M) + Ct-DNA	**8.25**	**7.91**	**10.41**	**10.02**
11	4MVQT (9.09 x 10^{-4} M) + Ct-DNA	**4.17**	**3.05**	**3.45**	**4.45**
12	4MVQT (1.98 x 10^{-4} M) + Ct-DNA	**2.93**	**2.38**	**3.75**	**3.20**
13	DMTQ (1 x 10^{-3} M) + Ct-DNA	**17.93**	**13.57**	**19.47**	**18.10**
14	DMTQ (9.09 x 10^{-4} M) + Ct-DNA	**4.21**	**3.69**	**4.43**	**5.46**

15	DMTQ (1.98 x 10^{-4} M) + Ct-DNA	**1.39**	**2.72**	**2.40**	**3.61**
16	DDDS (1 x 10^{-3} M) + Ct-DNA	**6.10**	**5.54**	**4.86**	**5.64**
17	DDDS (9.09 x 10^{-4} M) + Ct-DNA	**3.27**	**3.20**	**3.05**	**3.63**
18	DDDS (1.98 x 10^{-4} M) + Ct-DNA	**2.50**	**2.63**	**2.48**	**2.53**

In the case of amino chloro benzo phenones ACBP and its derivatives 6CPVQ, DCPVQ the results of DNA binding study reveal a shift in their OD values as concentration of the compound decreases. They show a bathochromism and hypochromism in the absorption implying the binding to be intercalated mode .

The amino nitro benzophenone ANBP and its derivatives 6NPVQ, 6NCPVQ, 6NPVQT show a decrease in OD values as the concentration was decreased. They are good intercalators to DNA. It is clear from the absorption peaks that the parent compound and derivatives shows bathochromism and hypochromism. Especially 6NPVQT act as good intercalators with DNA.

Table 6. Absorbance of samples in terms of optical density for 2-ABP

S.No	Sample	OD 260/280
1	2-ABP (1 x 10^{-3} M)	4.60
2	2-ABP (9.09 x 10^{-4} M)	4.08
3	2-ABP (1.98 x 10^{-4} M)	2.75
4	4PVQ (1 x 10^{-3} M)	0.77
5	4PVQ (9.09 x 10^{-4} M)	2.04
6	4PVQ (1.98 x 10^{-4} M)	44.72
7	2CPVQ (1 x 10^{-3} M)	0.65
8	2CPVQ (9.09 x 10^{-4} M)	0.92
9	2CPVQ (1.98 x 10^{-4} M)	0.44
10	4PVQT (1 x 10^{-3} M)	3.42
11	4PVQT (9.09 x 10^{-4} M)	5.46
12	4PVQT (1.98 x 10^{-4} M)	6.69

Table 7. Ratio of optical density values at 260 and 280nm obtained for the 2-ABP and its derivatives -Ct-DNA interaction

S.No.	**Sample**	**OD 260/280**			
		1hr	**2hr**	**3hr**	**4hr**
1	2-ABP (1 x 10^{-3} M) +Ct-DNA	**2.28**	**2.16**	**2.26**	**2.30**
2	2-ABP (9.09 x 10^{-4} M) + Ct-DNA	**2.25**	**0.81**	**1.82**	**2.22**
3	2-ABP (1.98 x 10^{-4} M) + Ct-DNA	**1.19**	**0.91**	**1.04**	**1.23**
4	4PVQ (1 x 10^{-3} M) +Ct-DNA	**1.19**	**1.85**	**1.87**	**2.02**
5	4PVQ (9.09 x 10^{-4} M) + Ct-DNA	**2.31**	**1.87**	**1.95**	**2.17**
6	4PVQ (1.98 x 10^{-4} M) + Ct-DNA	**2.41**	**1.89**	**1.78**	**2.49**
7	2CPVQ (1 x 10^{-3} M) + Ct-DNA	**0.11**	**0.39**	**0.51**	**0.49**
8	2CPVQ (9.09 x 10^{-4} M) + Ct-DNA	**3.41**	**5.46**	**3.72**	**4.92**
9	2CPVQ (1.98 x 10^{-4} M) + Ct-DNA	**1.97**	**2.23**	**2.17**	**2.26**
10	4PVQT (1 x 10^{-3} M) + Ct-DNA	**2.19**	**3.40**	**3.33**	**3.57**
11	4PVQT (9.09 x 10^{-4} M) + Ct-DNA	**2.72**	**2.58**	**2.80**	**2.59**
12	4PVQT (1.98 x 10^{-4} M) + Ct-DNA	**3.07**	**1.99**	**2.85**	**2.75**

Table 8. Absorbance of samples in terms of optical density for ACBP series

S.No	Sample	OD 260/280
1	ACBP (1 x 10^{-3} M)	3.65
2	ACBP (9.09 x 10^{-4} M)	3.07
3	ACBP (1.98 x 10^{-4} M)	2.42
4	6CPVQ (1 x 10^{-3} M)	4.45
5	6CPVQ (9.09 x 10^{-4} M)	3.55
6	6CPVQ (1.98 x 10^{-4} M)	2.19
7	DCPVQ (1 x 10^{-3} M)	8.04
8	DCPVQ (9.09 x 10^{-4} M)	18.86
9	DCPVQ (1.98 x 10^{-4} M)	-2.47

Table 9. Ratio of optical density values at 260 and 280nm obtained for the ACBP and its derivatives -Ct-DNA interaction

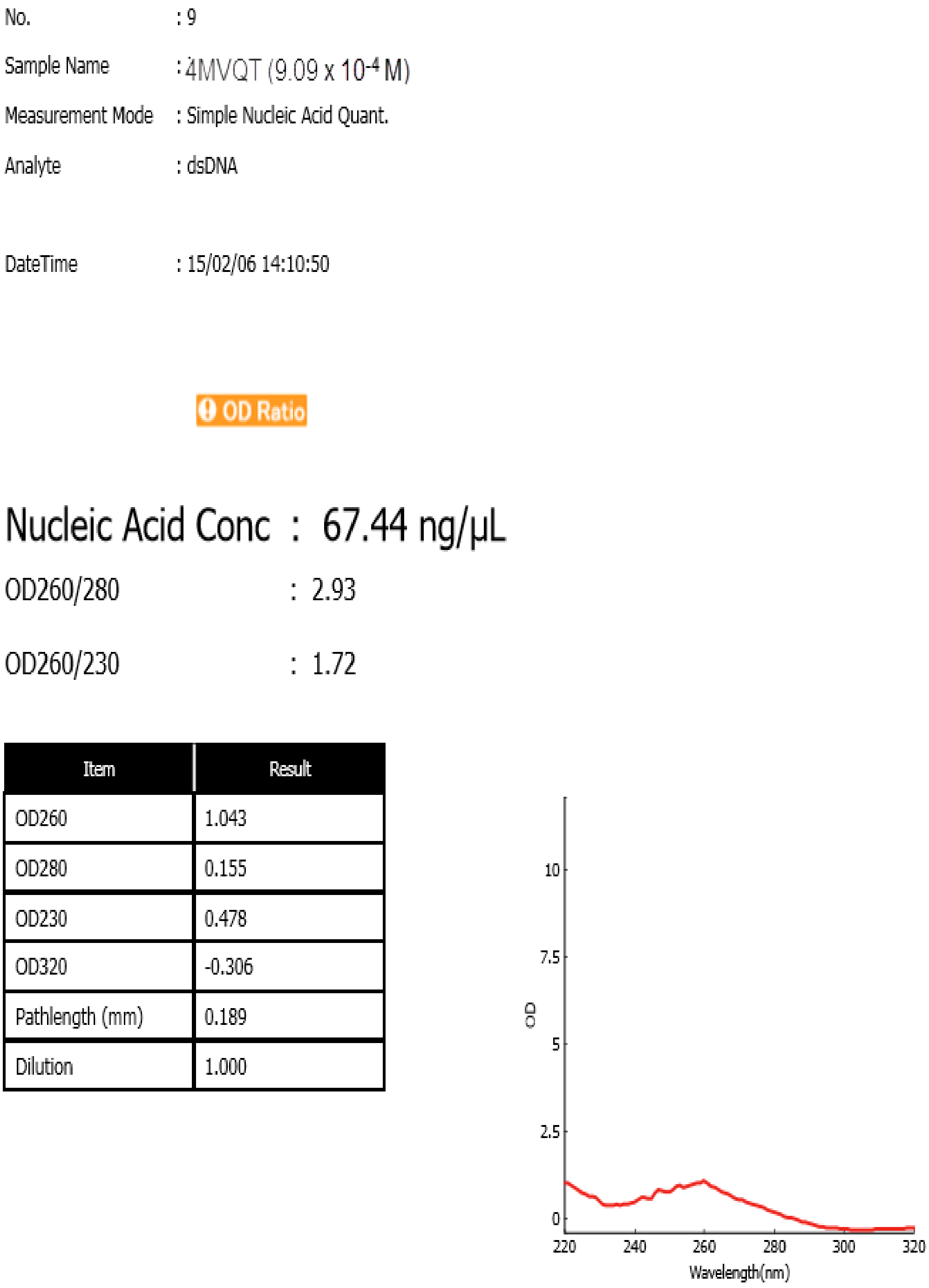
S.No.	Sample	OD 260/280			
		1hr	2hr	3hr	4hr
1	ACBP (1 x 10^{-3} M) +Ct-DNA	**2.18**	**2.20**	**2.25**	**2.07**
2	ACBP (9.09 x 10^{-4} M) + Ct-DNA	**2.22**	**2.14**	**2.54**	**2.16**
3	ACBP (1.98 x 10^{-4} M) + Ct-DNA	**2.02**	**1.76**	**2.08**	**1.86**
4	6CPVQ (1 x 10^{-3} M) +Ct-DNA	**2.94**	**3.09**	**2.89**	**3.14**
5	6CPVQ (9.09 x 10^{-4} M) + Ct-DNA	**2.86**	**2.66**	**2.64**	**3.49**
6	6CPVQ (1.98 x 10^{-4} M) + Ct-DNA	**2.59**	**2.16**	**2.34**	**2.40**
7	DCPVQ (1 x 10^{-3} M) + Ct-DNA	**7.13**	**7.06**	**6.73**	**7.83**
8	DCPVQ (9.09 x 10^{-4} M) + Ct-DNA	**4.45**	**3.10**	**3.40**	**3.33**
9	DCPVQ (1.98 x 10^{-4} M) + Ct-DNA	**1.93**	**1.78**	**1.83**	**1.77**

Table 10. Absorbance of samples in terms of optical density for ANBP and its derivatives

S.No	Sample	OD 260/280
1	ANBP (1 x 10^{-3} M)	-1.62
2	ANBP (9.09 x 10^{-4} M)	-1.61
3	ANBP (1.98 x 10^{-4} M)	-3.02
4	6NPVQ (1 x 10^{-3} M)	-0.74
5	6NPVQ (9.09 x 10^{-4}M)	-0.94
6	6NPVQ (1.98 x 10^{-4}M)	-1.56
7	6NCPVQ (1 x 10^{-3} M)	0.66
8	6NCPVQ (9.09 x 10^{-4} M)	-0.01
9	6NCPVQ (1.98 x 10^{-4} M)	3.36
10	6NPVQT (1 x 10^{-3} M)	2.17
11	6NPVQT (9.09 x 10^{-4}M)	-49.58
12	6NPVQT (1.98 x 10^{-4} M)	0.32

Table 11. Ratio of optical density values at 260 and 280nm obtained for the ANBP and its derivatives -Ct-DNA interaction

S.No.	Sample	OD 260/280			
		1hr	2hr	3hr	4hr
1	ANBP (1 x 10^{-3} M) +Ct-DNA	**2.22**	**2.02**	**2.19**	**2.24**
2	ANBP (9.09 x 10^{-4} M) + Ct-DNA	**2.52**	**2.45**	**2.07**	**2.57**
3	ANBP (1.98 x 10^{-4} M) + Ct-DNA	**2.19**	**1.82**	**2.32**	**2.15**
4	6NPVQ (1 x 10^{-3} M) +Ct-DNA	**21.66**	**-21.89**	**18.11**	**-33.92**
5	6NPVQ (9.09 x 10^{-4} M) + Ct-DNA	**9.88**	**10.26**	**14.44**	**10.15**
6	6NPVQ (1.98 x 10^{-4} M) + Ct-DNA	**3.21**	**2.48**	**2.08**	**1.99**
7	6NCPVQ (1 x 10^{-3} M) + Ct-DNA	**0.86**	**0.77**	**0.75**	**0.92**
8	6NCPVQ (9.09 x 10^{-4} M) + Ct-DNA	**1.23**	**0.97**	**1.11**	**1.08**
9	6NCPVQ (1.98 x 10^{-4} M) + Ct-DNA	**1.84**	**1.21**	**1.51**	**1.57**
10	6NPVQT (1 x 10^{-3} M) + Ct-DNA	**2.67**	**2.67**	**2.82**	**2.87**
11	6NPVQT (9.09 x 10^{-4} M) + Ct-DNA	**2.11**	**2.61**	**2.78**	**2.46**
12	6NPVQT (1.98 x 10^{-4} M) + Ct-DNA	**2.25**	**2.11**	**2.48**	**2.38**



No. : 9

Sample Name : 4MVQT (9.09 x 10^{-4} M)

Measurement Mode : Simple Nucleic Acid Quant.

Analyte : dsDNA

DateTime : 15/02/06 14:10:50

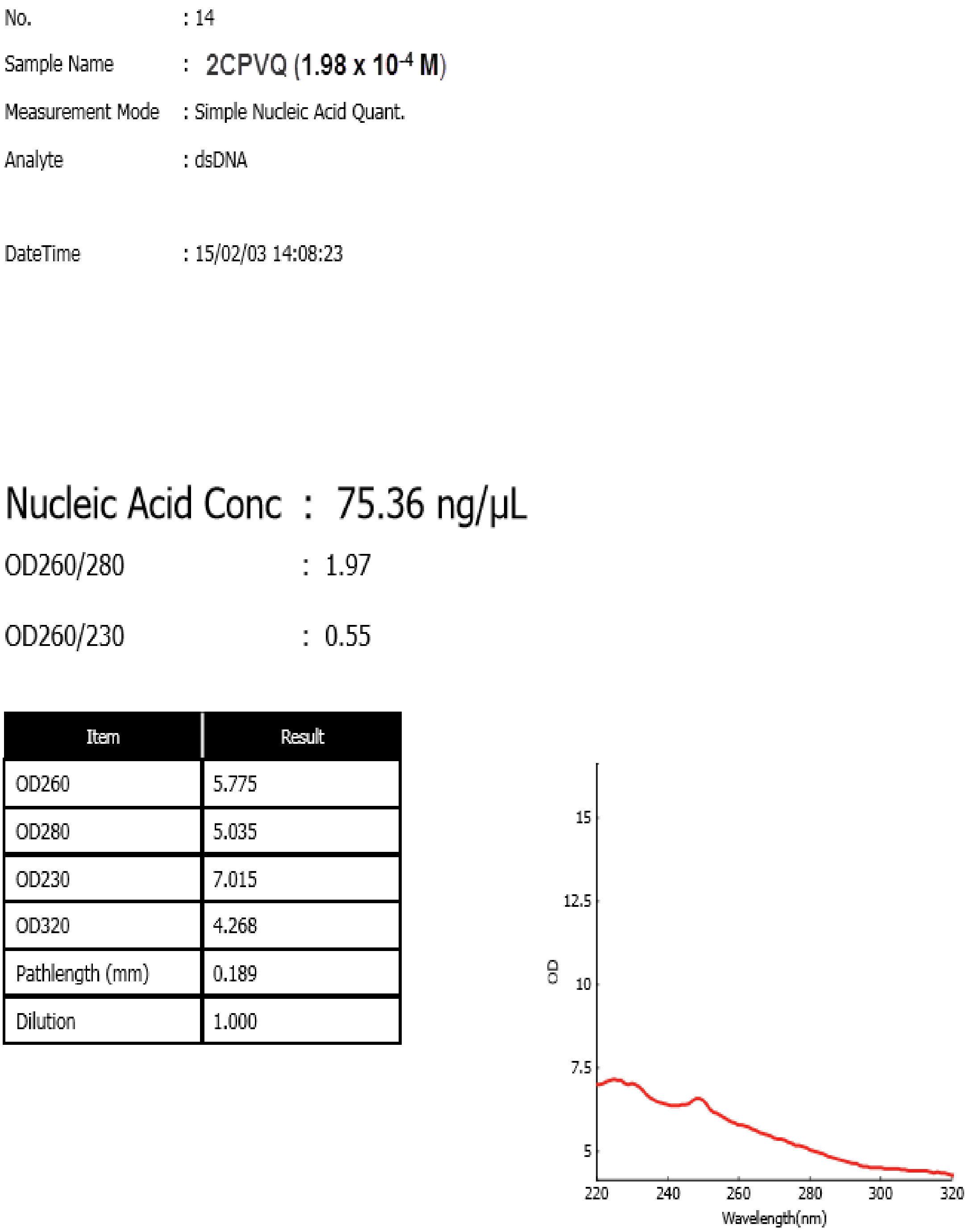
Nucleic Acid Conc : 67.44 ng/µL

OD260/280 : 2.93

OD260/230 : 1.72

Item	Result
OD260	1.043
OD280	0.155
OD230	0.478
OD320	-0.306
Pathlength (mm)	0.189
Dilution	1.000

Figure 18. Absorption spectrum of 4MVQT(9.09 x 10^{-4} M)after interaction with Ct-DNA



No. : 14

Sample Name : 2CPVQ (1.98 x 10^{-4} M)

Measurement Mode : Simple Nucleic Acid Quant.

Analyte : dsDNA

DateTime : 15/02/03 14:08:23

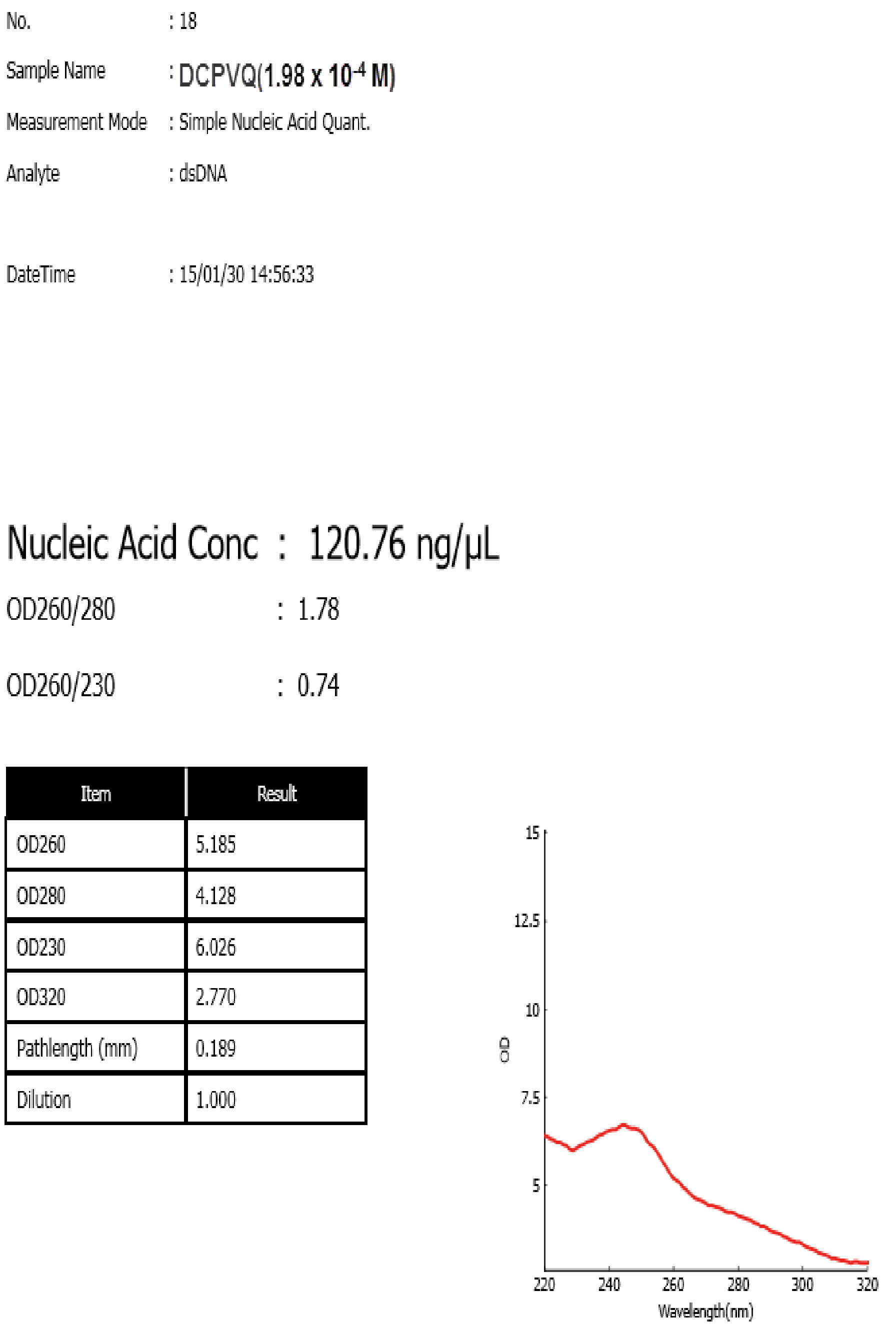
Nucleic Acid Conc : 75.36 ng/μL

OD260/280 : 1.97

OD260/230 : 0.55

Item	Result
OD260	5.775
OD280	5.035
OD230	7.015
OD320	4.268
Pathlength (mm)	0.189
Dilution	1.000

Figure 19. Absorption spectrum of 2CPVQ(1.98 x 10^{-4} M) after interaction with Ct-DNA



No. : 18

Sample Name : DCPVQ(1.98 x 10^{-4} M)

Measurement Mode : Simple Nucleic Acid Quant.

Analyte : dsDNA

DateTime : 15/01/30 14:56:33

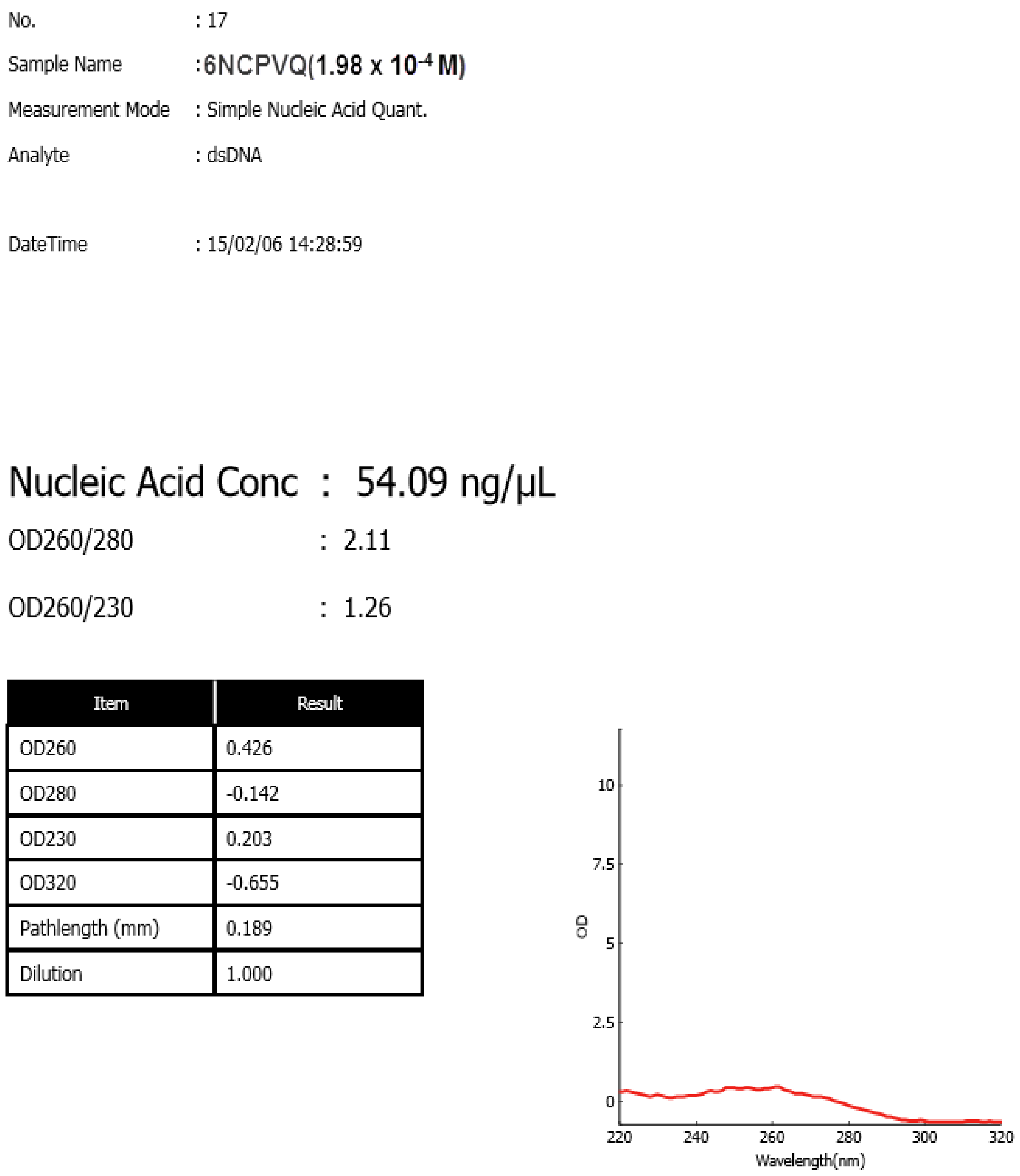
Nucleic Acid Conc : 120.76 ng/µL

OD260/280 : 1.78

OD260/230 : 0.74

Item	Result
OD260	5.185
OD280	4.128
OD230	6.026
OD320	2.770
Pathlength (mm)	0.189
Dilution	1.000

Figure 20. Absorption spectrum of DCPVQ(1.98 x 10^{-4} M) after interaction with Ct-DNA



No. : 17

Sample Name :6NCPVQ(1.98 x 10^{-4} M)

Measurement Mode : Simple Nucleic Acid Quant.

Analyte : dsDNA

DateTime : 15/02/06 14:28:59

Nucleic Acid Conc : 54.09 ng/μL

OD260/280 : 2.11

OD260/230 : 1.26

Item	Result
OD260	0.426
OD280	-0.142
OD230	0.203
OD320	-0.655
Pathlength (mm)	0.189
Dilution	1.000

Figure 21. Absorption spectrum of 6NCPVQ (1.98 x 10^{-4} M) after interaction with Ct-DNA

A facile way to establish interaction between the DNA and the drug is to examine the shifting of the position of the maximum of this band from when the ligand is free in solution to when the ligand is bound with the DNA. It has been assumed that the magnitude of this shifting could be interpreted as an indication of the strength of the interaction between the DNA structure and the ligand considered (**Sun et al., 2011; Jaumot and Gargallo, 2012; Wei et al,2010; Bhadra and Kumar,2011**). To sum up, in the present study, the results of the DNA binding study reveals all the synthesized compounds to be good DNA intercalators.

4.3 Photovoltaic application with the synthetic compopunds.

The second phase of the present study focused on the photovoltaic application with the synthetic heterocyclic compounds. Here an attempt is made to fabricate solar cells using four compounds 4MVQ, 6NPVQ, 6NCPVQ and DDDS. The reason for choosing the above four compounds is that they give a broad band in UV-visible spectra. The methodology followed is already explained in the materials and method chapter. The Current voltage characteristics obtained for the solar cells with four heterocyclic compounds is given in **Table 12.**

The obtained current and voltage are from approximately 3µl of compound. From the obtained values it is evident that the synthetic compounds are capable of producing large amount of current with minimum amount of compounds. The reason for the decrease in current and voltage when compared with other solar cells is that the size of the cell,the minimum amount of dye used and the decrease in thickness of the coating. The present study proves the ability of the organic compounds which reveal good absorption in the UV-visible spectroscopic techniques to act as good sensitizers and hence dyes in the fabrication of solar cells.

Table 12. Current, Voltage characteristics obtained for the solar cells

S. No	**Sample**	**Current (µA)**			**Voltage(V)**		
		Before exposing	5 min after exposing	15 min after exposing	Before exposing	5min after exposing	15 min
1	4MVQ	0.82	0.85	1.05	0.0126	0.0346	0.0423
2	6NPVQ	0.59	0.62	0.65	0.0039	0.0043	0.0061
3	6NCPVQ	0.13	0.26	0.27	0.0049	0.0053	0.0055
4	DDDS	0.49	0.59	1.04	0.0024	0.0046	0.0051

Further work with applied voltage and studying its open circuit potential and arriving at the current voltage characteristics is warranted. Calculation of fill factor and efficiency is recommended as future work.

SUMMARY AND CONCLUSION

5. SUMMARY AND CONCLUSION

The conclusion of the present study reveals the following points

- The microwave assisted synthesis of heterocyclic compounds gives a good yield than the conventional method of synthesis.
- The time needed for the reaction to yield the product is very much lesser than the time consumed in the conventional synthesis.
- The compounds are characterized using UV-visible spectroscopy and IR spectroscopy.
- The *In vitro* DNA binding studies of the synthesized compounds was determined from the OD values and the variation in the shift of absorption band before and after interaction with DNA
- Both hypsochromic and bathochromic shifts were obtained for all the synthetic compounds
- The compounds intercalate with DNA even at lower concentration of the compounds. This trend was seen in all the derivatives.
- As time increases the OD value decreases in most of the compounds.
- The study demonstrates quinolone compounds and its derivatives to be good intercalators with DNA.
- The UV-Visible spectra of selected compounds such as 4MVQ, 6NPVQ, 6NCPVQ, DDDS gives a broad band in the region between 200 and 450.
- This motivated to follow the second phase of the study.
- An attempt was made to fabricate economical solar cells with the synthesized compounds.
- The four compounds gave appreciable current and voltage with the minimum amount of compound.
- The photovoltaic performance can be improved by increasing the thickness of the sensitizers used such as TiO_2, the size of the cell(Photo active area) also by increasing the quantity of dye used for coating.

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