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All praise and glory to Allah the almighty who alone made this small objective to be accomplished. I feel honored and privileged to glorify his name in the sincerest way through this small accomplishment and ask him to accept my efforts.

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Marwa

Summary

Summary

This thesis consists of synthesis of five new highly conjugated dimeric and trimeric azo compounds which were synthesized according to the schemes shown below.

- The first compound A1 consist of π -conjugated compounds containing 1,3,4-oxadiazole as the central units with terminal azo phenyl.
- The second compound A2 consist of π-conjugated compounds containing 1,2,4triazole (V) as the central units with terminal azo phenyl group and lateral *p*bromobenzylideneamino group, as shown below (scheme 2).
- Compound V 4,4⁻(*p*-bromobenzylideneamino)-5,5⁻-mercapto[bis-1,2,4-triazole-3-yl]phenyl was prepared as shown in scheme (3).
- The third compound A3 consist of π -conjugated compounds containing pyromelittic diimide as the central units with terminal azo phenyl group, as shown below (scheme 4).
- The fourth compound A4 consist of π-conjugated compounds derived from 3,5dihydroxy benzoic acid, as shown below (scheme 5).
- The fifth compound A5 consist of trimeric π -conjugated compounds derived from 1,3,5-trihydroxy benzene, as shown below (scheme 6).

- All the synthesized compounds were characterized using FTIR and CHNS-O analysis and some of them by ¹HNMR

- The liquid crystalline properties of synthesized compounds which were verified using differential scanning calorimeter (DSC) and hot- stage polarizing optical microscope (POM) were discussed.

- The compounds show photoluminescence properties in the organic solution at room temperature, with the fluorescence band centered around 400 nm.





Scheme 1: The synthetic pathway for compound A1.



Scheme 2: The synthetic pathway for compound A2.





Scheme 3: The synthetic pathway for compound 4,4⁻(p-bromobenzylideneamino)-5,5⁻ mercapto[bis-1,2,4-triazole-3-yl]phenyl V.



Scheme 4: The synthetic pathway for compound A3.

Summary



Scheme 5: The synthetic pathway for compound A4.



Scheme 6: The synthetic pathway for compound A5.

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List of Abbreviations	
LC	Liquid crystal
LCs	liquid crystals
S	Order parameter
n	director
ND	Discotic nematic liquid crystal phase
Sm	Smectic phase
Ν	Nematic phase
номо	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
PL	Photoluminescence
РОМ	Polarizing Optical Microscope
DSC	Differential scanning calorimeter
S _N i	Internal nucleophilic substitution mechanism
Cr	Crystal
Ι	Isotropic liquid

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Chapter One

Introduction and Literature

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1.1 Liquid crystal

1.1.1 Definition

Liquid crystal molecule is an intermediate state of a matter, in between the liquid and the crystal. It must possess some typical properties of a liquid (e. g. fluidity, inability to support shear, formation and coalescence of droplets) as well as some crystalline properties (anisotropy in optical, electrical, and magnetic properties, periodic arrangement of molecules in one spatial direction, etc)⁽¹⁾

The distinguishing characteristic of the liquid crystalline state is the tendency of mesogens to point along a common axis called the director (n) which is a unit vector and is called the liquid crystal director ⁽²⁾. In the solid state, molecules are highly ordered and have little translational freedom. The characteristic orientational order of the liquid crystal state is between the solid and liquid phases and this is the origin of the term mesogenic state, used synonymously with liquid crystal state⁽³⁾. The alignment of the molecules for each phase showed in the figure 1.1.



Figure 1.1: Alignment of the molecules for solid, liquid crystal and liquid phase⁽²⁾.

1.1.2 History of liquid crystal

In 1888, the Austrian chemist Friedrich Reinitzer⁽⁴⁾, working in the Institute of Plant Physiology at the University of Prague, discovered a strange phenomenon⁽⁵⁾. Reinitzer was conducting experiments on a cholesterol based substance trying to figure out the correct formula and molecular weight of cholesterol. When he tried to precisely determine the melting point, which is an important indicator of the purity of a substance, he was struck by the fact that this substance seemed to have two melting points. At 145.5°C the solid crystal melted into a cloudy liquid which existed until 178.5°C where the cloudiness suddenly disappeared, giving way to a clear transparent liquid. At first Reinitzer thought that this might be a sign of impurities in the material, but further purification did not bring any changes to this behavior ⁽⁵⁾. Puzzled by his discovery, Reinitzer turned for help to the German physicist Otto Lehmann, who was an expert in crystal optics. Lehmann became convinced that the cloudy liquid had a unique kind of order. In contrast, the transparent liquid at higher temperature had the characteristic disordered state of all common liquids. Eventually he realized that the cloudy liquid was a new state of matter and coined the name "liquid crystal," illustrating that it was something between a liquid and a solid, sharing important properties of both. In a normal liquid the properties are isotropic, i.e. the same in all directions. In a liquid crystal they are not; they strongly depend on direction even if the substance itself is fluid ⁽⁴⁾. In 1922 the French scientist Friedel⁽⁶⁾ produced the first classification scheme of LCs, dividing them into three different types of mesogens (materials able to sustain mesophases), based upon the level of order the molecules possessed in the bulk material:

- 1. Nematic (from the Greek word nematos meaning "thread" ⁽⁷⁾
- 2. **Smectic** (from the Greek word smectos meaning "soap")⁽⁷⁾
- 3. Cholesteric (better defined as chiral nematic) ⁽⁷⁾

1.2 Characterizing Liquid Crystals:

The following parameters describe the liquid crystalline structure:

- Orientational order: Measure of the tendency of the molecules to align along the director on a long-range basis.
- Positional order: The extent to which the position of an average molecule or group of molecules shows translational symmetry.
- Bond orientational order: Describes a line joining the centers of nearest-neighbor molecules without requiring a regular spacing along that line. Thus, a relatively long range order with respect to the line of centers but only short range positional order along that line.

Each of these parameters describes the extent to which the liquid crystal sample is ordered. *Positional order* refers to the extent to which an average molecule or group of molecules shows translational symmetry (as crystalline material shows). *Orientational order*, as discussed above,

represents a measure of the tendency of the molecules to align along the director on a long-range basis. *Bond Orientational Order* describes a line joining the centers of nearest-neighbor molecules without requiring a regular spacing along that line. Thus, a relatively long-range order with respect to the line of centers but only short range positional order along that line⁽⁷⁾. Most liquid crystal compounds exhibit polymorphism, or a condition where more than one phase is observed in the liquid crystalline state. The term mesophase is used to describe the "subphases" of liquid crystal materials. Mesophases are formed by changing the amount of



order in the sample, either by imposing order in only one or two dimensions, or by allowing the molecules to have a degree of translational motion.⁽⁸⁾

1.3 General types of liquid crystals:

Considering the geometrical structure of the mesogenic molecules, the liquid crystals can be grouped into several types. The liquid crystals derived from the rodshaped molecules (i.e., one axis is much longer than the other two) are called "calamities". The mesophases formed from disc-like molecules (i.e., one molecular axis is much shorter than the other two) are referred to as "discotics". However, the often used term 'discotic' intermediate between rod-like and disc-like molecules are the lath-like species⁽⁹⁾.



Figure 1.2: physical models. (a) rod-like, (b) Disc-like liquid crystal⁽¹⁰⁾

A mesogen is rigid rod-like or disc-like molecules which are components of liquid crystalline materials. It is sometimes difficult to determine whether a material is in a crystal or liquid crystal state. Crystalline materials demonstrate long range periodic order in three dimensions. By definition, an isotropic (Having properties that are the same regardless of the direction of measurement. In the isotropic state, all directions are indistinguishable from each other) liquid has no orientational order. Substances that aren't as ordered as a solid, yet have some degree of alignment are properly called liquid crystals. The term crystallinity implies the presence of three-dimensional order on the level of atomic dimensions. In polymers, the range of order may be as small as about 2 nm in one (or more) crystallographic direction(s) and is usually below 50 nm in at least one direction. Polymer crystals frequently do not display the perfection that is usual for low-molecular mass substances. Polymer crystals that can be manipulated individually are often called polymer single crystals. To quantify just how much order is present in a material, an order parameter (S) is defined. S describes the orientational order of liquid crystalline material, allowing for the individual orientational deviation of the molecules from the director, which represents the average over the collection. Traditionally, the order parameter is given as follows:





Figure 1.3: Representation of order parameter⁽⁸⁾.

Where θ ; is the angle between the director and the long axis of each molecule. The brackets denote an average over all of the molecules in the sample. In an isotropic liquid, the average of the cosine terms is zero, and therefore the order parameter is equal to zero. For a perfect crystal, the

order parameter evaluates to one. Typical values for the order parameter of a liquid crystal range between 0.3 and 0.9, with the exact value a function of temperature, as a result of kinetic molecular motion.

This order parameter is highly dependent on the temperature of the sample. Compounds capable forming liquid crystals must be have several properties such as a rigid center region and flexible tail. The following is general structure of liquid crystal ⁽¹⁰⁾.



Figure 1.4: General structure of the mesogenic molecule ⁽⁹⁾

Ring Unit:



1.4 Phases of liquid crystal:

The various liquid-crystal phases (called mesophases) can be characterized by the type of ordering. One can distinguish positional order (whether molecules are arranged in any sort of ordered lattice) and orientational order (whether molecules are mostly pointing in the same direction), and moreover order can be either short-range (only between molecules close to each other) or long-range (extending to larger, sometimes macroscopic, dimensions). Most thermotropic LCs will have an isotropic phase at high temperature. That is that heating will eventually drive them into a conventional liquid phase characterized by random and isotropic molecular ordering (little to no long-range order), and <u>fluid</u>-like flow behavior. Under other conditions (for instance, lower temperature), a LC might inhabit one or more phases with significant anisotropic orientational structure and short-range orientational order while still having an ability to flow⁽¹¹⁾.

The ordering of liquid crystalline phases is extensive on the molecular scale. This order extends up to the entire domain size, which may be on the order of micrometers, but usually does not extend to the macroscopic scale as often occurs in classical crystalline solids. However some techniques, such as the use of boundaries or an applied electric field, can be used to enforce a single ordered domain in a macroscopic liquid crystal sample. The ordering in a liquid crystal might extend along only one dimension, with the material being essentially disordered in the other two directions⁽¹²⁾.

1.4.1 Thermotropic liquid crystals:

Thermotropic phases are those that occur in a certain temperature range. If the temperature rise is too high, thermal motion will destroy the delicate cooperative ordering of the LC phase, pushing the material into a conventional isotropic liquid phase. At too low temperature, most LC materials will form a conventional crystal⁽¹³⁾. Many thermotropic LCs exhibit a variety of phases as temperature is changed. For instance, a particular type of LC molecule (called <u>mesogen</u>) may exhibit various smectic and nematic (and finally isotropic) phases as temperature is increased.

1.4.1.1 Nematic phase:

In a nematic phase, the *calamitic* or rod-shaped organic molecules have no positional order, but they self-align to have long-range directional order with their long axes roughly parallel⁽¹⁴⁾. Thus, the molecules are free to flow and their center of mass positions are randomly distributed as in a liquid, but still maintain their long-range directional order. Most nematics are uniaxial: they have one axis that is longer and preferred, with the other two being equivalent (can be approximated as cylinders or rods). Nematics have fluidity similar to that of ordinary (isotropic) liquids but they can be easily aligned by an external magnetic or electric field.



Figure 1.5: Molecular arrangement of nematic phase.

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1.4.1.2 Smectic phases

The smectic phases, which are found at lower temperatures than the nematic, form well-defined layers that can slide over one another in a manner similar to that of soap. The word "smectic" originates from the Latin word "smecticus", meaning cleaning, or having soap like properties.^[15] The smectics are thus positionally ordered along one direction. In the Smectic A phase, the molecules are oriented along the layer normal, while in the Smectic C phase they are tilted away from the layer normal. These phases are liquid-like within the layers. There are many different smectic phases, all characterized by different types and degrees of positional and orientational order⁽¹⁴⁾.



Figure 1.6: Schematic of alignment in the smectic phases.

1.4.1.3 Cholesteric

The cholesteric phase is like the nematic phase in having longrange orientation order and no long-range order in positions of the centers of mass of molecules. It differs from the nematic phase in that the director varies in direction throughout the medium in a regular way. The configuration is precisely what one would obtain by twisting about the x axis a nematic initially aligned along the y axis⁽¹⁴⁾.





Figure 1.7: Schematic of alignment in the cholestric phase.

1.4.1.4 Blue phases

Blue phases are liquid crystal phases that appear in the temperature range between a chiral nematic phase and an isotropic liquid phase. Blue phases have a regular three-dimensional cubic structure of defects with lattice periods of several hundred nanometers. Although blue phases are of interest for fast light modulators or tunable photonic crystals, they exist in a very narrow temperature range, usually less than a few kelvin. Recently the stabilization of blue phases over a temperature range of more than 60 K including room temperature (260-326 K) has been demonstrated⁽¹⁵⁾. Blue phases stabilized at room temperature allow electro-optical switching with response times of the order of 10^{-4} s⁽¹⁶⁾.



Figure 1.8: blue phase.

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U	

1.4.1.5 Discotic phases

Disk-shaped Liquid crystal molecules can orient themselves in a layer-like fashion known as the discoticnematic phase. If the disks pack into stacks, the phase is called a discotic columnar. The columns themselves may be organized into rectangular or hexagonal arrays. Chiral discotic phases, similar to the chiral nematic phase, are also known. The simplest discotic phase is the discoticnematic (designated N_D); it is the least ordered and the least viscous. There is no long-range positional correlation. The columnar phase consists of discs stacked one on top of the other a periodically to form liquid-like columns; the different columns constituting a two dimensional lattice⁽¹⁷⁾.



Figure 1.9: Discotic phase

1.4.2 Lyotropic liquid crystals

A lyotropic liquid crystal consists of two or more components that exhibit liquid-crystalline properties in certain concentration ranges. In the lyotropic phases, solvent molecules fill the space around the compounds to provide fluidity to the system⁽¹⁸⁾. In contrast to thermotropic liquid crystals, these lyotropics have another degree of freedom of concentration that enables them to induce a variety of different phases.

A compound that has two immiscible hydrophilic and hydrophobic parts within the same molecule is called an amphiphilic molecule. Many



amphiphilic molecules show lyotropic liquid-crystalline phase sequences depending on the volume balances between the hydrophilic part and hydrophobic part. These structures are formed through the micro-phase segregation of two incompatible components on a nanometer scale. Soap is an everyday example of a lyotropic liquid crystal.



Figure 1.10: Structure of lyotropic liquid crystal. The red heads of surfactant molecules are in contact with water, whereas the tails are immersed in oil (blue).

1.5 Luminescence

Luminescence is the radiative emission of ultraviolet, visible or infrared photons from an electronically excited species to return to its ground state. In the ground state, the bonding electrons occupy the highest occupied molecular orbital (HOMO). When sufficient energy is provided to a molecule, its electrons can overcome the energy barrier required to move from their ground state (HOMO) to a higher energy level (LUMO). The excited molecule may be organic, inorganic or organometallic in nature. These excited molecules can partially lose the energy radiatively (emit light radiations) when electrons go from the excited state back to the ground state and this phenomenon of light luminescence⁽¹⁹⁾. The called various emission is luminescence phenomena are given names based on the type of radiation used to excite the emission table $1.1^{(20)}$.



Luminescence phenomena	Methods of excitation
Photo-luminescence	Light or photons
Bioluminescence	Bio-chemical energy
Sono luminescence	Sound waves
Electro-Luminescence	Electric field
Chemi-Luminescence	Chemical energy
Tribo –Luminescence	Mechanical energy
Cathodo-Luminescence	Electrons or cathode rays
Radio Luminescence	Nuclear radiation or Ionizing radiation
Florescence	Ionizing radiation ,UV and visible light
Phosphorescence	Ionizing radiation ,UV and visible light
Thermoluminsecence	Ionizing radiation ,UV and visible light

Table 1.1: Luminescence phenomena and the methods of excitation⁽²⁰⁾.

1.5.1 Photoluminescence

Luminescence in solids is the phenomenon in which electronic states of solids are excited by some energy from an external source and the excited energy is released as light. When the energy comes from short wavelength light, usually ultraviolet light the phenomenon is called photoluminescence (PL). PL in solids is classified in view of the nature of the electronic transitions producing the luminescence⁽²¹⁾. The present discussion is related to photoluminescence in which a species is excited by absorption of photon and subsequently the excited species loses part of the absorbed energy radiatively resulting in luminescence. The further classified photoluminescence is into fluorescence or phosphorescence depending on whether the excited species responsible for emission is in the singlet or triplet state.





Figure 1.11: Different electronic state in molecules

Organic molecules contain an even number of electrons and have a singlet ground state with a net spin of zero. The ground singlet state is usually labeled as S0 and the first, second and higher electronic excited singlet states are represented by S1, S2 and Sn respectively, with n = 3, 4, 5 and so on. A molecule exhibits a singlet state when there is no net electronic spin associated with the state i.e. all of the spins are paired. The spin multiplicity formula (M = 2S + 1) gives the number of the states which can arise, where the 'S' is the total spin quantum number. In the case when all the electrons of a molecule are spin-paired, S = 0, the spin multiplicity is 1, which represents the singlet state. In contrast, the excited states in which the two electron spins are parallel have an overall spin momentum (S = 1) a spin multiplicity = 3. Having unpaired electrons, they exhibit magnetic properties and, in a magnetic field, split into three sub-states of slightly different energies. These states are therefore referred as "triplet" states" and are - 14possible T1, T2, and so on, where 'T' indicates that there are three - 14possibilities of spin orientate ion of the two unpaired electrons⁽¹⁹⁾.



1.6 Literature Survey

In (2010) a new mesomorphic azo compounds (I) distinguished by the presence of diverse substituents on a central benzene nucleus and study their liquid crystalline properties ⁽²²⁾.



X = H, OH, CH₃, F, Cl

(I)

A series of ortho-metallated Pd and Pt complexes containing dimeric liquid crystals Schiff base as N-benzoyl thiourea (II) and cyclometallated ligands (III) derivatives as co-ligands were prepared and investigated for their liquid crystalline properties⁽²³⁾.



(II)

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In (2011) a new type of liquid crystal (LC) heterogeneous system that contains hydrogen-bonded polymer-azo-dye complexes (VI) at a low concentration was prepared ⁽²⁴⁾.



(VI)

In (2013) a chiral four ring unsymmetrical bent-core liquid crystals (V) derived from 3-amino-2-methylbenzoic acid have been designed and synthesized with an imine, ester and photochromic azo linking moieties. These hockey-stick shape resembling bent molecules possess an alkoxy chain at one end of the molecule and methyl or methoxy group at the other end⁽²⁵⁾.





(V)

Photosensitive soft matter based upon guest-host liquid crystal systems was prepared by mixing azobenzene-containing mesogens with the nematic liquid crystal 4-butyl-cyclohexane carboxylic acid 4-pentyloxy-phenyl ester⁽²⁶⁾ (VII).



(VII)

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A series of elongated azo esters containing three rings with methyl moiety as one of the terminal carbon chain and various substituents X (X= H,CH₃,OCH₃,NO₂,Cl) at the other end of the molecule have been isolated (VIII) to explain the dipole moment on the liquid crystal phases⁽²⁷⁾.



(VIII)

In (2014) the synthesis of two new poly(amidoamine) dendrimers (IV) from first generation modified with 1,8-naphthalimide fluorescent units is described. Their photophysical characteristics have been investigated in organic solvents of different polarity in order to investigate their sensor potential. Selectivity for detection of cuprum cations has been demonstrated⁽²⁸⁾.



(IV)

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Xiao-Zhi He, et.al. separated a new series of cholesteric fluorated branched-arm liquid crystals compound (MFA_1-MFA_4), with isosorbide as chiral core. Four precursors of branched-arm FA_1-FA_4 were obtained firstly and then were esterized separately with isosorbide to get four chiral branched-arm liquid crystalline (MFA_1-MFA_4). The structures and properties were characterized by conventional spectrum methods, thermal analysis and texture analysis. The results showed that FA_1-FA_4 all were nematic phase with schlieren, threaded-like or droplet texture⁽²⁹⁾.



Figure 1.12: Branched arm liquid crystal⁽²⁹⁾.
1.7 Aim of work

The specific objectives of this work include:

- Synthesis of new luminescent containing highly conjugated azo compounds.
- Synthesis of new bent shaped liquid crystals based on the 2,5disubstituted oxadiazole and triazole.
- Structural characterization of the intermediates and final compounds through infrared spectroscopy (FTIR), proton nuclear magnetic resonance spectroscopy (¹H-NMR) and elemental analysis.
- Studies the thermal and mesomorphic properties of the aimed compounds through DSC and POM.
- Investigation of the photophysical properties of the final compounds using UV-Vis absorption and emission techniques.

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Chapter two

Experimental

2.1 Chemicals

The following chemicals were used directly from their mentioned suppliers; without further purification:

Materials	Supplied from	Purity %
Di methyl terephthaliat	Fluka	99
Hydrazine hydrate	BDH	97
Potassium hydroxide	BDH	98
Carbon disulfide	Merck	99
Absolute ethanol	BDH	99.9
4-aminoazobenzene	Fluka	97
Hydrochloric acid	BDH	99
Sodium nitrile	BDH	98
Sodium hydroxide	BDH	96.7
Benzoic acid	BDH	98
Thionyl chloride	Merck	97
Dimethylformamide	BDH	99
(DMF)		
Pyridine	Merck	98
Acetic acid	Fluka	99
Pyromelitticdiimide	Fluka	99
Phoroglucinol anhydrous	Fluka	99
3,5-dihydroxy benzoic acid	Merck	98

Table 2.1: Chemicals and their manufactures

2.2 Instruments and Requirements

• Infrared Spectrophotometer (IR)

FTIR spectra recorded in the range (4000-400) 1 cm using potassium bromide disk on the Model 8300 FTIR instrument Shimadzu Spectrophotometer, Japan. Analysis is performed at department of chemistry, college of science /Al Nahrain University.

¹H Nuclear magnetic resonance spectrometer (NMR):

Hydrogen Nuclear Magnetic Resonance (¹HNMR) was recorded spectra on a Brüker ACF 300 spectrometer at 300 MHz, using DMSO or deutrated chloroform as solvent with TMS as an internal standard, in the university of Exeter, England.

• Elemental Analysis:

Elemental analysis (CHNS-O) was carried out using EURO EA elemental analyzer instrument. The analyses were carried out at department of chemistry, college of science /Al Nahrain University.

Melting point:

Uncorrected melting point were Recorded on hot stage Gallen Camp melting point apparatus (UK).

• Differential scanning calorimeter (DSC):

Transition temperatures and enthalpies were scanned by LINSEIS DSC PT-1000 differential scanning calorimeter with a heating rate of 10.0°C/min in air and it was calibrated with indium (156.6°C, 28.45 J/g) at department of chemistry, college of science /Al Nahrain University.

• Hot stage Polarizing Microscope:

Liquid crystalline properties were investigated by using a (Meiji MT9000) Polarizing Optical Microscope attached to an INSTEC Hot stage. The texture of the compounds were observed using polarized light with crossed polarizers, the sample being prepared as a thin



film sandwiched between a glass slide and a cover. A camera (Lumenera) was installed on the polarizing microscope. The analysis were carried out at department of chemistry, college of science /Al Nahrain University.

Spectrofluorometer

Fluorescence spectra were recorded by using excitation wavelengths corresponding to the peaks of their absorption diagrams by using (F96-pro). The analysis were carried out Laser engineering department at Al-Nahrain University.

2.3 Preparations and syntheses methods

2.3.1 Synthesis of phenylene (1-azobenzen)(4,4^{*}-azobenzoic acid)I ⁽³⁰⁾:

4-Amino azo benzene (0.01mol, 1.97 g) was dissolved in distilled water acidified with 3drops of conc. hydrochloric acid. The nitrous acid was prepared using sodium nitrite (0.01 mol, 0.7 g) in distilled water then added to the above mixture drop by drop in ice bath. After that resulting solution was added to the solution of 10 % sodium hydroxide and benzoic acid (0.01 mol, 1.22 g) dropwise, at (0 – 5 °C).

2.3.2 Synthesis of phenylene (1-azobenzen)(4,4^{*}-azobenzoyl chloride II⁽³¹⁾:

Phenylene (1-azobenzen)(4,4⁻-azobenzoic acid) (0.01 mol, 3.3 g) was refluxed with thionyl chloride (10 ml) for 2 hrs. The excess of thionyl chloride was distilled off by simple distillation and the obtained acid chloride was directly use.



2.3.3 Preparation of terephthalicdihydrazide III

Dissolve dimethyl terephthalate (0.01 mol, 1.94 g) in absolute ethanol 15 ml, then hydrazine hydrate (97 %, 2 ml) was added and reflex for 4 hrs. After that the solution was cooled to the room temperature and filtered, a white solid was obtained.

2.3.4 Preparation of 5,5`-dimercapto[bis-1,3,4-oxadiazole-2-yl]phenyl IV⁽³²⁾:

Dissolve KOH (0.015 mol, 0.89 g) in absolute ethanol (7.5 ml) then added to a mixture of dimethyl terephthalic dihydrazine (0.01 mol, 1.5 g) and carbon disulfide (1.5 ml), in ice bath till the yellow precipitate was obtained which was dissolved in absolute ethanol (10 ml), then reflux about 7hrs. The obtained solid was filtered and dried to obtain the desired product.

2.3.5 Synthesis of compound A1:

Phenylene (1-azobenzen)(4,4⁻-azobenzoyl chloride II (0.02 mol, 6.96 g) and (0.01 mol, 2.78 g) of 5,5⁻-dimercapto[bis-1,3,4-oxadiazole-2-yl]phenyl IV was dissolved in 20 ml pyridine. The mixture was stirred for 3h in an ice bath then poured onto cold water acidified with acetic acid and filtered to obtain the desired product.

2.3.6 Synthesis of 4,4`-(p-bromobenzylideneamino)-5,5`mercapto[bis-1,2,4-triazole-3-yl]phenyl V⁽³²⁾:

Compound V was synthesized according to literature, by the reaction of compound IV with excess of hydrazine hydrate (97 %) which gave 4-amino-1,2,4-triazole-2-thiol, and the last prepared compound undergoes condensation reaction with 4-bromobenzaldehyde to afford compound V.



2.3.7 Synthesis of compound A2:

(0.02 mol, 6.96 g) of phenylene (1-azobenzen)(4,4 -azobenzoyl chloride II and (0.01 mol, 5.84 g) of 4-4 -bromobenzylideneamino-1,2,4-tiazole-2-thiol V was dissolved in 20 ml pyridine. The mixture was stirred for 3hrs. in an ice bath then poured onto cold water acidified with acetic acid and filtered. The product was washed with cold water, filtered and dried to obtain the desired product.

2.3.8 Synthesis of compound A3:

(0.02 mmol, 6.96 g) of phenylene (1-azobenzen)(4,4⁺-azobenzoyl chloride II and (0.01mol, 2.16 g) of pyromelittic diimide was dissolved in 20 ml of pyridine. The mixture was stirred for 3hrs. in an ice bath then poured onto cold water acidified with acetic acid and filtered. The product was washed with cold water, filtered and dried to obtain the desired product.

2.3.9 Synthesis of compound A4:

(0.02 mmol, 6.96 g) of phenylene (1-azobenzen)(4,4`-azobenzoyl chloride II and (0.01mol, 1.54 g) of 3,5-di hydroxy benzoic acid was dissolved in 20 ml pyridine. The mixture was stirred for 3hrs. in an ice bath then poured onto cold water acidified with acetic acid and filtered. The product was washed with cold water, filtered and dried to obtain the desired product.

2.3.10 Synthesis of compound A5:

(0.03 mmol, 10.44 g) of phenylene (1-azobenzen)(4,4⁻-azobenzoyl chloride II and (0.01mol, 1.26 g) of phloroglucinol anhydrous was dissolved in 20 ml pyridine. The mixture was stirred for 3hrs. in an ice bath then poured onto cold water acidified with acetic acid and filtered.



The product was washed with cold water, filtered and dried to obtain the desired product.

Table 2.2 shows the melting points and % yield of the synthesized compounds.

Comp.No.	Yield %	m.p (°C)
I	74	150-152
II	90	85-93
III	92	196-197
IV	70	224-226
V	82	174-176
A1	63	135-140
A2	58	200-210
A3	64	170-180
A4	60	187 -192
A5	71	204-208

 Table 2.2: Melting points and % yield of synthesized compounds.

Chapter Three

Results & Discussion

3.1 Synthesis and characterization of compound A1:

3.1.1 Synthesis of phenylene (1-azobenzene)-4-(3-azobenzoyl chloride)(II):

The title compound was synthesized as shown in scheme (3.1):



Scheme 3.1: The synthetic pathway for phenylene (1-azobenzen)-4-(3-azobenzoyl chloride) II.

The reactions to compound II involve two steps, firstly preparation of diazonium salt and secondly coupling reaction with benzoic acid as shown below scheme (3.2):





Scheme 3.2: Mechanism steps for preparation of phenylene (1-azobenzen)-4-(3-azobenzoic acid) I.

Figure 3.1 shows the FTIR spectrum of **I** using KBr disc which showed the following characteristic absorption bands: 3260 cm^{-1} and 1690 cm^{-1} that could be attributed to O – H stretching and carbonyl of carboxyl group respectively and bands at 1512 cm⁻¹ due to aliphatic N = N stretching of azo group, while the out of plane bending of *meta*- and *Para*-disubstituted benzene ring appeared at 782, 702 and 846 cm⁻¹ respectively.





Compound (I) was reflux with thionyl chloride to afford phenylene (1-azobenzen)-4-(3-azobenzoyl chloride (II) according to SN_i mechanism as shown below scheme (3.3):



Scheme 3.3: Mechanism steps for preparation of phenylene (1-azobenzen)-4-(3-azobenzoyl chloride) II.



Figure (3.2) show the FT-IR spectrum of compound (II), which showed the disappearance of hydroxyl group stretching band and shifting the carbonyl group from 1690.4 to 1782.2 cm⁻¹ which is good evidence for preparation the desired compound.



Figure 3.2: FTIR spectrum of phenylene (1-azobenzen)-4-(3-azobenzoyl chloride) II.

3.1.2 Synthesis and characterization of compound A1:

The sequence steps of synthesis of A1 are shown in the Scheme below scheme (3.4):



Scheme 3.4: The synthetic pathway for compound A1.

The synthetic steps involve the preparation of $5,5^{-}$ -dimercapto[bis-1,3,4-oxadiazole-2-yl]phenyl (IV)⁽³²⁾ by, firstly the preparation of terephthalic dihydrazide (III) which was prepared by the reaction of dimethyl terephthalate with hydrazine hydrate. The spectrum figure (3.3), (KBr disc cm⁻¹), shows the appearance of the N - H group of hydrazide at 3459.4, 3272.9 and 3165.1 for asymmetrical and symmetrical stretching. The spectrum also show bands at 1685.6, 1598.8 785, 698 and 825.5 due to C=O (amide I), N - H bending (amide II), and out of plane bending of *meta-* and *para-* disubstituted respectively.





Figure 3.3: FTIR spectrum of Terephthalic dihydrazide (III).

Compound (III) was treated with carbon disulphide in basic media to obtained 5,5⁻dimercapto[bis-1,3,4-oxadiazole-2-yl]phenyl (IV) according to a reported method of Young and Wood⁽³³⁾.

The FTIR spectrum of compound (IV) figure (3.4) shows the disappearance of N – H stretching bands and appearance of bands at 1608.5 and 1251.7 due to C = N and C–O–C of (oxadiazole ring). The spectrum revealed a sulphohydryl absorption band S – H at 2740.2 cm⁻¹ and an N – H absorption stretching band at 3201 cm⁻¹ and a new band at 1350 cm⁻¹ due to C = S was observe due to the tiol – thion equilibrium⁽³⁴⁾:





(Thion) II

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Figure 3.4: FTIR spectrum of 5,5`-dimercapto[bis-1,3,4-oxadiazole-2-yl]phenyl (IV).

Reaction of compound (IV) with phenylene (1-azobenzen)(4,4`-azobenzoyl chloride), led to compound (A1), the mechanism of synthesis is shown below scheme (3.5):





Scheme 3.5: Mechanism steps for preparation of compound A1.

The structure of this compound was elucidated on the basis of elemental analysis (table 3.1), FTIR and ¹HNMR spectral data. The FTIR spectrum of this compound figure (3.5) showed the disappearance of S-H stretching band and detection of strong C=O stretching band at 1720 cm⁻¹ are evidence for the carbonyl group. The FTIR spectrum showed bands at 3065, 1620, 1589, 1506, 829, 782 and 692 that could be attributed to C-H aromatic stretching, C = N stretching, C=C stretching, N = N stretching and out of plane bending of *p*- and *m*- disubstituted respectively.



Figure 3.5: FTIR spectrum of 1,4-phenylene-5-bis[phenylene (1-azobenzen)-4-(3azothiobenzoate) A1.

¹H-NMR (DMSO-d6, δ in ppm); figure (3.6): 6.94 (d, 4H, arom. H) for the benzene ring fall between two oxadiazole ring, 8.14-8.17 (m, 8H, arom. H) for the two phenyl group attached to thio ester group, 8.11-8.13 (d, 8H, arom. H) for the two phenyl group fall between two azo group while the terminal two mono substituted benzene ring gave multiplate at 7.46-7.93 (10 H).



Figure 3.6: ¹HNMR spectrum of compound A1.

3.2 Synthesis and characterization of compound A2:

The sequence steps for the synthesis of A1 are shown in the Scheme (3.6) below:



Scheme 3.6: The synthetic pathway for compound A2.

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The synthetic steps involve the preparation of 4,4`-(*p*-bromobenzylideneamino)-5,5`-mercapto[bis-1,2,4-triazole-3-yl]phenyl (V)⁽³²⁾, as shown in the following scheme (3.7):



Scheme 3.7: The synthetic pathway for compound 4,4`-(p-bromobenzylideneamino)-5,5`mercapto[bis-1,2,4-triazole-3-yl]phenyl V.

Compound V was prepared by the reaction of compound (IV) with hydrazine hydrate to achieve $4,4^-amino-5,5^-mercapto[bis-1,2,4-triazole-3-yl]phenyl$ followed by condensation reaction with 4-bromobenzaldehyde to achieve $4,4^-(p-bromobenzylideneamino)-5,5^-mercapto[bis-1,2,4-triazole-3-yl]phenyl (V). The$



spectrum figure (3.7), (KBr disc cm⁻¹), showS the appearance of bands at 3110.2, 2724.8, 1602.4 and 841.1 which could be assigned to v C - H of azomethane group, v S - H, v C = C and out of plane bending of *para*- disustituted benzene ring.



Figure 3.7: FTIR spectrum of 4,4`-(p-bromobenzylideneamino)-5,5`-mercapto[bis-1,2,4triazole-3-yl]phenyl (V).

Reaction of compound II with 4,4^{\component}-(*p*-bromobenzylideneamino)-5,5^{\component}mercapto[bis-1,2,4-triazole-3-yl]phenyl (V) lead to the formation of the dimer A2. The constitution of this product was supported by elemental analysis (table 3.1), FTIR and ¹H-NMR spectra. The FTIR spectrum figure (3.8), showed the disappearance of S-H stretching band and detection of strong C=O stretching band at 1723.4 cm⁻¹ are evidence for the carbonyl group. ¹H-NMR (DMSO-d6, δ in ppm); figure (3.9): showed a signals between 7.10-7.14 (two doublet, 4H, arom. H) for the benzene ring fall between two triazole ring, 8.22-8.28 (m, 8H, arom. H) for the two phenyl group attached to thio ester group, 8.18 (d, 8H, arom. H) for the two phenyl



group fall between two azo group while the terminal two mono substituted benzene ring gave multiplate at 7.35-7.38 (10 H). the azo methane proton appear as singlet at 8.1 (2H), 7.5-7.9 (d, 8H, arom.) for the bromo *p*-benzene ring.



Figure 3.8: FTIR spectrum of A2.



Figure 3.9: ¹HNMR spectrum of compound A2

3.3 Synthesis and characterization of compound A3:

Combination between compound (II) and pyromelittic diimide in the presence of pyridine as proton acceptor lead to obtain compound A3. The reaction steps shown in scheme 3.8:

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D	40	



Scheme 3.8: The synthetic pathway for compound A3.

The structure of this compound was elucidated on the basis of elemental analysis (table 3.1), FTIR and ¹H-NMR spectral data. The FTIR spectrum of this compound figure (3.10), revealed the disappearance of N – H amide stretching and the appearance of C = O stretching at 1718.6 and 1705.4 cm⁻¹. ¹H-NMR (DMSO-d6, δ in ppm); figure (3.11): 6.94 (s, 2H, arom. H) for the pyromelittic benzene ring, 8.10-8.16 (m, 8H, arom. H) for the two phenyl group attached to amide group, 8.17-8.19 (d, 8H, arom. H) for the two phenyl group fall between two azo group while the terminal two mono substituted benzene rings gave multiplate at 7.39-7.52 (10 H).

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D	41	











3.4 Synthesis and characterization of compound A4:

The reaction of II with 3,5-dihydroxy benzoic acid yielded compound A4, as shown below scheme (3.9):



Scheme 3.9: The synthetic pathway for compound A4.

The reaction of two equivalents of compound (II) with 3,5-dihydroxy benzoic acid gave compound A4, the structure of this compound was elucidated on the basis of elemental analysis (table 3.1), FTIR and ¹HNMR spectra. The FTIR spectrum figure (3.12) of this compound revealed the disappearance of phenolic hydroxyl group and the appearance of carbonyl ester group at 1742.5 cm⁻¹. ¹HNMR (DMSO-d6, δ in ppm); figure (3.13): 7.20-7.24 (s, 3H, arom. H) for the benzene ring fall between two ester groups, 8.05-8.08 (m, 8H, arom. H) for the two phenyl group fall between two azo group while the terminal two mono substituted benzene ring gave multiplate at 7.38-7.42 (10 H). The proton of carboxylic acid group occurs as singlet at 12.11.









Figure 3.13: ¹HNMR spectrum of compound A4.

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3.5 Synthesis and characterization of compound A5:

The reaction of II with 1,3,5-trihydroxy benzene yielded compound A5, as shown in scheme (3.10) below;



Scheme 3.10: The synthetic pathway for compound A5.

The reaction of three equivalents of compound (II) with 1,3,5-trihydroxy benzene gave compound A5, the structure of this compound was elucidated on the basis of elemental analysis (table 3.1), FTIR and ¹HNMR spectra. The FTIR spectrum figure (3.14) of this compound revealed the disappearance of phenolic hydroxyl group and the appearance of carbonyl ester group at 1738.6 cm⁻¹. ¹HNMR (CDCl₃, δ in ppm); figure (3.15): 6.97-6.99 (s, 3H, arom. H) for the benzene ring fall between three ester groups, 7.25-7.30 (m, 15H, arom. H) for the protons in three terminal aromatic rings. The spectrum also showed signal at 7.61-7.77 (m, 12H, arom. H) for the protons near to the azo group in three aromatic rings fall between ester group and azo group and, 8.13-8.15 (dd, 12H, arom. H) for the protons of three phenyl group fall between two azo group.





Figure 3.14: FTIR spectrum of compound A5.



Figure 3.15: ¹HNMR spectrum of compound A5.

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D	46	

Comp.	Formula	%	C	%	H	%	N	0/	ώS
No.		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
Ι	C19H14N4O2	69.09	68.98	4.24	4.17	16.96	16.84	-	-
IV	C10H6N4O2S2	43.16	42.97	2.15	2.12	20.14	20.11	23.02	23.07
V	C24H16Br2N8S2	45.00	45.02	2.50	2.49	17.50	17.54	10.00	9.88
A1	C48H30N12O4S2	63.85	63.64	3.32	3.35	18.62	18.70	7.09	7.12
A2	C62H40Br2N16 O2S2	58.86	59.03	3.16	3.11	17.72	17.65	5.06	5.09
A3	C48H28N10O6	68.57	68.87	3.33	3.36	16.66	16.71	-	-
A4	C45H30N8O6	69.40	69.29	3.85	3.81	14.39	14.18	-	-
A5	C57H42N12O6	69.09	70.03	4.24	4.27	16.96	17.01	-	-

Table 3.1: Elemental Analysis (CHNS-O) for synthesized compounds.

 Table 3.2: Characteristic FTIR absorption bands of synthesized compounds (A1-A5).

Comp.No	υ C-H aroma.	vN = N	υ C=O	υ C=C	υ C - Ο	Others
A1	3065.3	1445.2	1720.3 (acid)	1589.2	1294.2 (cyclic)	
A2	~ 3050.0	1440.5	1723.4 (thio ester)	1598.0	-	3111.5 & 16121.2 (CH=N)
A3	~ 3050.0	1438.9	1718.6 &1705.4 (amide and imide	1608.5	1172.6	
A4	-	1441.6	1742.5 (ester), 1698.8 (acid)	1569.9	1256.7	3312.5 (COOH)
A5	3054.6	1447.1	1741.7 (ester)	1608.5	1251.7 & 1172.6	

3.6 Thermotropic Liquid Crystalline Properties of synthesized compounds (A1-A5):

Terminal substituents play a significant role in promoting liquid crystalline properties in a mesogen ⁽³⁵⁾. Thermotropic properties of the synthesized compounds



were examined using hot-stage polarizing microscope and differential scanning calometry (DSC).

3.6.1 Study the texture by means of hot-stage polarizing optical microscope (POM):

Liquid crystalline properties of compound A1 was examined by means of hot stage polarizing microscope. Compound A1 showed a fan- shape smectic phase, figure 3.16.

The presence of an oxadiazole ring into the principle structure of compound A1 could cause considerable changes of polarity, polarizability and geometry of the molecules and influenced the type and the phase transition temperature of the mesophases⁽³⁶⁾. The fall of oxadiazole ring as a central linker will cause some deviation from linearity⁽³⁷⁾, this may cause the molecule to be assumed a layer crystal lattice conducive to smectic behaviour.



Figure 3.16: Fane shape smectic texture of compound A1 at 135°C (magnification 10 × 10).

The mesomorphic properties of compound A2 showed Schlieren texture of the SmC phase when examined using hot stage polarizing microscope, figure 3.17.

The slightly higher smectic thermal stabilities of compound A2 may probably due to the presence of the -CH = N-⁽³⁸⁾central linkage which is more coplanar than the -COS- central linkage and allows packing of the molecules such that the smectic



thermal stabilities of compound A2 become higher than those of compound A1. The thermal stability of a mesophase is a more important factor in relating mesomorphic behavior to chemical constitution, since the temperature range of a mesophase may be determined partly by the unpredictable nature of the crystal-mesophase temperature ⁽³⁹⁾.



Figure 3.17: Schlieren texture of the SmC phase of compound A2 at 205°C (magnification 10× 10).

The microscopic observation of compound A3 showed nematic mesophase, figure 3.18; this could be attributed to lateral/ terminal interaction⁽⁴⁰⁾. The azo linker group generally will have a higher transition temperature when compared to the amide linker group (CONH). The strength of the terminal group enhanced the nematic properties.





Figure 3.18: Spherical droplets nematic phase of compound A3 at 174 °C (magnification 10 × 10).

Liquid crystalline properties of compound A4 also was examined by means of hot stage polarizing microscope. Compound A4 showed smectic mesophase, Figure 3.19. The observation of smectic mesophase can construe to the presence of carboxylic group which have the potential to form intermolecular hydrogen bonding⁽⁴¹⁾ as shown below:







Figure 3.19: Batonnet texture of the SmC phase of compound A4 at 190°C (magnification 10× 10).

To make a comparison, we synthesized compound A5 as a trimer. The microscopic examination of compound A5 gave discotic nematic (N_D) phase, figure 3.20.



Figure 3.20: Discotic nematic texture of compound A5 at 206°C (magnification 10×10).

3.6.2 Examination the mesomorphic properties using Differential scanning calorimetry :

The polarizing optical microscopic observations for compounds (A1-A5) were supported by the DSC thermogram which is shown in figure (3.21) below.





Figure 3.21: Differential scanning thermograms of compounds A1 - A5 respectively as a function of temperature for the second heating and cooling cycles (at scan rate 10 °C min⁻¹).

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On heating of the synthesized compounds (A1-A5), two different peaks can be observed in the heating cycle at 135.0°C, 205°C, 174°C, 190°C and 206°C, respectively, where crystal (Cr) is melted to a smectic mesophase (Sm) for compounds (A1, A2 and A4) or to a nematic mesophase (N) (A3 and A5). Further heating, to 250°C, isotropic (I) liquid formed. All of the peaks indicated the endothermic energy absorbed the crystal molecules to break the intermolecular forces between molecules apart⁽⁴²⁾.

Comp. No.	Melting point°C	Transition
A1	135-140	C → Sm
A2	200-210	C → Sm
A3	170 -180	$C \rightarrow N$
A4	187-192	C → Sm
A5	205-210	$C \rightarrow N$

Table 3.3: Melting points and type of transition for compounds A1-A5.

C = Crystal; Sm = Smectic ; N = Nematic; I = Isotropic liquid.

3.7 Absorption and Photoluminescence study:

Absorption and Photoluminescence spectrum were studied for the synthesized material to determine the interesting spectral range of operation of these materials to select them for the specific optoelectronic devices.

The whole compounds **A1-A5** was found to be intensely fluorescent and emit in the yellowish-green region of the visible spectrum under an UV light. To study influence of the molecular structure on their photophysical properties, their absorption and emission spectra were measured in ethanol solutions using UV-absorption and fluorescence spectroscopic techniques. At the beginning, it was


important to determine the absorption spectrum for the selected material. Then, the fluorescence spectra were measured using fluorescence spectrometer. The spectra were recorded by measuring the emissions from the molecule which have been excited either by the whole range radiation directly from the lamp or using different filters. Finally, it was necessary to analyze these spectra to decide the important range for further examinations and future applications.

3.7.1 Absorption Spectra:

The absorption spectra for A1- A5 were recorded by using photospectrometer in the range (190-1200 nm). As seen in figure 3.22 which shows the UV-absorption spectra of the final compounds, all compounds showed bands with maximum absorptions (λ_{max}) between 426 and 437 nm.



Figure 3.22: UV-vis absorption spectra of the fluorescent compounds A1-A5 taken in ethanol.

It can be seen that the absorption spectra of the studied samples are mainly in the ultraviolet range and short wavelengths from the visible range.



Obviously, that compound A5 has wider absorption range than the others, this can explain due to the highly conjugation of molecule and high $\pi - \pi^*$ transition. The reason of the broadening spectra in all studied samples comes from the fact the molecules have high molecular weight⁽⁴³⁾. The interaction between the ethanol and the molecules could also cause a broadening spectrum.

3.7.2 Photoluminesce Spectra:

The photoluminesce spectra or the fluorescence measurements have been studied using the fluorescence spectrometer in the range (200-900 nm).

Figure 3.23 shows the emission spectrum for the Xe lamp used to excite the studied samples. If we compared this spectrum by the spectra emitted from compounds A1-A5 as shown in figure 3.24, we observe that the fifth sample (A5) is highly absorb at the UV and blue range. There is high emission spectrum at the visible range between (480-800 nm). While the absorption edge for the same sample ends at 570 nm. That is fit to the literature⁽⁴⁴⁾ where the overlap between the absorption spectrum and the emission spectrum is corresponding to the decay within the higher energy band.



Figure 3.23: The emission spectrum for the Xe lamp used to excite the studied samples.

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Figure 3.24: The photoluminescence spectra for compounds A1 - A5.

Compounds A3 and A4 showed a wide range fluorescence spectrum (400-800), this emission showed also wide range overlap with the absorption spectra which explains the low photoluminesce intensity. The reason behind this overlap can be either the effect of the interaction between the molecule and the solvent (Ethanol) or because a strong self-absorption which is corresponding to a broad band. As we see from the photoluminesce spectra there is a similarity in behavior for compounds A1/A2 and also for compounds A3/A4, this could be assigned to the rapprochement in molecular structures.



Conclusion

These compounds were designed to exhibit liquid-crystalline and luminescent properties. Some of the compounds showed mesomorphism. The preliminary results suggest a general pattern that increasing the length of the rigid part of the molecule increases the tendency to form a mesophase. Another general conclusion that can be drawn from these results is that an increase in the molecular length also enhances the thermal stability of the mesophases due to increased rigidity which facilitates a better orientational order and molecular packing in the mesophases.

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تضمنت الرسالة تحضير خمس مركبات جديدة عالية التبادل ثنائية وثلاثية تحتوي على مجموعة آزو والتي تم تحضيرها حسب المخططات الموضحة ادناه.

- تضمن المركب الاول عالي التبادل A1 على مجموعة 4،3،1- اوكسادايزول كوحدة مركزية مع مجموعة الآزو الطرفية.



Scheme 1: The synthetic pathway for compound A1.

- المركب الثاني A2 احتوى على مجموعة 4،2،1- ترايازول كوحدة مركزية بالضافة الى مجموعة الآزو الطرفية ومجموعة جانبية تمثلت بالمجموعة بارا-برموبنزليدين امينو.



Scheme 2: The synthetic pathway for compound A2.

- تم تحضير المركب V حسب المخطط الموضح:



- يحتوي المركب الثالث A3 على مجموعة بايروملتك ثنائي الايمايد كوحدة مركزية بالأضافة الى مجموعة الآزو الطرفية، كما موضح ادناه:



Scheme 3: The synthetic pathway for compound A3.

المركب الرابع A4 يحتوي على وحدة مركزية مشتقة من 5،3-ثنائي هيدروكسي حامض البنزويك،
 كما موضح ادناه:



Scheme 4: The synthetic pathway for compound A4.

- المركب الخامس A5 ثلاثي التعويض تم تحضيره من 5،3،1-ثلاثي هيدروكسي بنزين ، كما موضح

ادناه:



Scheme 5: The synthetic pathway for compound A5.

- جميع المركبات المحضرة تم تشخيصها باستخدام مطياف الاشعة تحت الحمراء FTIR وتحليل العناصر CHNS-O والبعض منها تم تشخيصه باستخدام مطيافية الرنين النووي المغناطيسي لذرة الهيدروجين HNMR.
- تم تحديد الصفات البلورية السائلة للمركبات المحضرة بأستخدام مسعر المسح التفاضلي DSC وكذلك بأستخدام مجهر الضوء المسقطب المزود بمسخن حراري POM.
- أظهرت المركبات المحضرة خصائص التلالئ الفوتوني في محاليل عضوية وفي درجة حرارة الغرفة،
 تراوحت حزمة التفلور حوالي 400 نانومتر.

