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**PYRAZOLINE-BASED ORGANIC EMITTERS AS COLOR-
CONVERSION MATERIALS FOR LED APPLICATIONS**

MASTER OF SCIENCE

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ABSTRACT

PYRAZOLINE-BASED ORGANIC EMITTERS AS COLOR- CONVERSION MATERIALS FOR LED APPLICATIONS

MSC THESIS

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In this study, in the first step, some novel pyrazoline derivatives comprising aryl groups at positions 1 and 3, and a vinyl-1,2,4-oxadiazole group at position 5, were successfully synthesized. The molecular structures of the compounds were elucidated and confirmed using infrared (IR), magnetic nuclear resonance (NMR), and mass spectroscopy techniques. In the second part, the photophysical properties of fluorescent pyrazoline-based compounds were investigated by linear absorption, steady-state fluorescence, and time-resolved fluorescence (TRF) spectroscopies. The results showed that the electron-withdrawing ability of the substituent at position 3 has a crucial role in the spectral position of the fluorescence (FL) emission wavelength of the compounds in the solution. However, there is no significant contribution to the FL emission by the substituents on the 1,2,4-oxadiazole group at position 5. In addition, the pyrazoline-based compound having -CN group at position 3 has been found to have the highest fluorescence quantum yield (FL-QY) reaching about 86% in the solution. It was also found that the compounds are strongly affected by the polarity of the solvent, which results in a redshift in fluorescence emission with decreasing FL-QYs. These results reveal the intramolecular charge transfer (ICT) characteristics of the compounds. On the other hand, the synthesized compounds exhibit photoluminescence (PL) emission in the solid state, covering the regions from blue to red of the electromagnetic spectrum. It was found that all compounds have low PL QYs in the solid state, in which the highest PL QY was measured to be 18.2%. The analysis of the TRF results has revealed that the nonradiative decay processes dominantly govern the emission kinetics of the compounds depending on the substituents. Furthermore, the monolith structure of some of the compounds, which were prepared under 80 kN to investigate color-conversion application, exhibited highly mechano-fluorochromic (MFC) properties. Here, it was found that their PL emission shifted about 70 nm to the longer-wavelength side of the spectrum. Finally, as a proof-of-concept demonstration, the synthesized pyrazoline derivatives were employed as a color-converter material on a light-emitting diode (LED).

KEYWORDS: Pyrazoline, 1,2,4-oxadiazoles, photophysical properties, fluorescence emission, solid-state emission, fluorescence quantum yield, fluorescence lifetime, solvent polarity effect, and color conversion LED

ÖZET

**LED UYGULAMALARI İÇİN RENK DÖNÜŞÜM MALZEMELERİ
OLARAK PİRAZOLİN TABANLI ORGANİK İŞIYICILAR
YÜKSEK LİSANS TEZİ
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Bu çalışmada, ilk aşamada, 1 ve 3 pozisyonlarında aril grupları ve 5 pozisyonunda vinil-1,2,4-oksadiazol grubu içeren bazı yeni pirazolin türevleri başarıyla sentezlendi. Bu bileşiklerin moleküler yapıları kızılötesi (IR), manyetik nükleer rezonans (NMR) ve kütle spektroskopisi teknikleri kullanılarak aydınlatıldı ve doğrulandı. İkinci bölümde floresan pirazolin bazlı bileşiklerin fotofiziksel özellikleri doğrusal absorpsiyon, kararlı durum floresans ve zamanla çözölmüş floresans (TRF) spektroskopileri ile araştırıldı. Sonuçlar, 3 pozisyonunda bulunan ikame edicinin elektron çekme yeteneğinin, bileşiklerin çözöcü içindeki floresans (FL) ışıma dalgaboyunun spektral konumunda çok önemli bir role sahip olduğunu göstermiştir. Ancak 5 pozisyonda bulunan 1,2,4-oksadiazol grubu üzerindeki ikame edicinin FL emisyonuna önemli bir katkısı bulunmamıştır. Ayrıca 3 pozisyonda -CN grubuna sahip olan pirazolin bazlı bileşiğin çözöcü içinde yaklaşık %86'ya ulaşan floresans kuantum verimi (FL-QY) ile en yüksek değere sahip olduğu bulunmuştur. Ayrıca bileşiklerin çözöcünün polaritesinden güçlü bir şekilde etkilendiği ve bunun FL-QY'lerin azalmasıyla birlikte floresans emisyonunda kırmızıya kaymaya neden olduğu da bulunmuştur. Bu sonuçlar bileşiklerin moleköl içi yük transferi (ICT) özelliklerini ortaya koymaktadır. Diğer taraftan sentezlenen bileşikler, katı halde, elektromanyetik spektrumun maviden kırmızıya kadar olan bölgelerini kapsayan fotoluminesans (PL) ışıması göstermektedirler. Tüm bileşiklerin katı halde düşük PL QY'da sahip olduğu bulundu; burada en yüksek PL QY %18.2 olarak ölçölmüştür. TRF sonuçlarının analizi, ikame edicilere bağılı olarak bileşiklerin ışıma kinetiğinin baskın olarak ışıınımsal olmayan bozunma mekanizmaları tarafından yönetildiğini ortaya çıkarmıştır. Ayrıca renk dönüşüm uygulamasını araştırmak amacıyla 80 kN altında hazırlanan bazı bileşiklerin monolit yapısı yüksek derecede mekano-florokromik (MFC) özellikler sergilemiştir. Burada PL ışımasının yaklaşık 70 nm kadar spektrumun daha uzun dalga boyu tarafına kaydığı bulunmuştur. Son olarak, bir kavram kanıtı gösterimi olarak, sentezlenen pirazolin türevleri, ışık yayan bir diyot (LED) üzerinde renk dönüştürücü malzeme olarak kullanılmıştır.

ANAHTAR KELİMELEER: Pirazoller, 1,2,4-oksadiazoller, fotofiziksel özellikler, floresan ışıma, katı hal ışıması, floresans kuantum verimi, floresans yaşam ömrü, çözöcü polaritesi etkisi ve renk dönüşümlü LED

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1. INTRODUCTION

The human population has been growing steadily over the last few centuries, and today the world population is more than three times larger than that in the mid-twentieth century. According to the 2022 report published by the Population Department of the United Nations Department of Economic and Social Affairs (UN DESA), although the growth rate of the world population slows down every year, the human population has reached approximately 8 billion on a global basis. Additionally, studies predict that the global population may reach approximately 8.5 billion in 2030 and 9.7 billion in 2050, increasing by 1.18 billion in the next two decades (1). This increasing trend in the human population also increases the need for energy. The International Energy Agency (IEA) and the Energy Information Administration (EIA), the world's two main energy agencies, state that the use of global energy will increase by approximately 50% by 2050 compared to 2020, based on the statistics published by UN DESA (2).

One of the factors that makes a significant contribution to global energy consumption due to the increasing human population is artificial lighting applications, which are indispensable in today's modern social life and one of the largest areas of electricity use in the world. According to the report published by the United Nations Environment Program (UNEP), approximately 20% of global electricity consumption and 6% of carbon dioxide emissions are due to artificial lighting (3). In addition, according to the 2022 report published by the IEA, the increase in energy consumed for lighting and the resulting carbon emissions continue (4). This reveals the importance of energy-saving lighting applications and ongoing studies in this field in ensuring energy efficiency in a global context. For this reason, solid-state lighting (SSL) technology is emerging today as an alternative to incandescent lamps, which are very poor in terms of energy efficiency, as well as fluorescent lamps, which are also traditional lighting systems and have reached saturation in terms of efficiency. The high efficiency provided by this lighting technology consisting of light-emitting diodes (LED) in both economic and energy consumption has been integrated into all areas where lighting technology is needed in daily life, such as general lighting in homes and offices, street lighting, automotive lighting, and backlighting in liquid crystal displays

(LCD) in a short time. According to a report on lighting published in 2022 by the International Energy Agency, more than 50% of the global lighting market uses LED technology (4). For this reason, research on methods and materials that will increase efficiency in terms of both energy and lighting in LED technology and applications has accelerated in recent years.

Since today's LED technology is based on epitaxial growth of semiconductor materials, an LED chip can only operate in a narrow radiation band. In other words, the color properties of LEDs can be adjusted thanks to the materials used in the LED chip structure. However, white light, one of the most important needs of daily life, cannot be obtained from a single LED source. This has led researchers to develop different approaches to obtaining white light from energy-efficient LEDs, and after the discovery of red (R), green (G), and blue (B) LEDs, white light production through the LEDs has become possible (5). It is achieved by combining LED chips that can glow in these three primary colors (R, G, and B), which are the components of white light, in a single configuration. Due to the different responses of each LED chip to different operating conditions, such as temperature and drive current, and the need for necessary optimization, this approach increases the commercial costs of LEDs to very high levels. For this reason, another method that is preferred more than RGB LEDs in both industry and academic research is phosphor-converted LEDs based on the principle of obtaining white light through color conversion using high-energy photons. Here, white light can be obtained by using luminescent color-converting materials integrated on LED chips that emit high-energy photons in the blue or violet region (5). Today, phosphors derived from rare earth elements are used in these LEDs. For example, a typical white light-producing color-conversion LED application uses a yellow phosphor (i.e., Cerium-doped Yttrium Aluminum Garnet, YAG:Ce^{3+}) dispersed in an optically transparent polymeric structure such as silicon, epoxy, or PDMS on a blue LED. This phosphor absorbs blue light and emits it in the green-red band range of the visible region of the electromagnetic spectrum (6). The blue light emitted from the LED chip is partly absorbed by the phosphor coating, while the other part is transmitted. As a result, the combination of blue light (from the LED chip), green light (from the phosphor), and red light (from the phosphor) allows to obtain white light (7–9). However, although this method is the most common white light

production method in LEDs, when the use of rare earth element ion-doped phosphors such as gadolinium, cerium, and terbium in LED chips (10) is evaluated in terms of cost and availability of raw materials, there is a need to develop new and efficient phosphors in this field.

In recent years, semiconductor colloidal nanocrystals have come to the forefront as color conversion materials to replace traditional phosphors in hybrid LED systems (11–14). However, in addition to the problems in large-scale and cost-effective production, toxic elements such as cadmium (Cd) and selenium (Se) found in the structure of especially efficient nanocrystals make these materials unsuitable for use in environmentally friendly devices (15,16). For hybrid LED systems, another important alternative is fluorescent organic compounds (17). In addition to their photophysical properties, fluorescent organic compounds stand out with their advantages, such as easy synthesis, low cost, and low toxicity compared to inorganic emitters. Furthermore, organic fluorescent materials also have the potential to reduce the LED industry's dependence on expensive, rare earth-containing materials. The optical properties of these compounds depend on the relevant electronic transitions, and structural design strategies can be used to fine-tune the optical properties of these materials. The emission kinetics of conventional organic molecules such as rhodamine, fluorescein, and BODIPY under photoexcitation are governed by optical transitions delocalized over the entire structure. On the other hand, in organic compounds consisting of electron-donating (donor, D) and electron-withdrawing (acceptor, A) groups, the emission generally results from intramolecular charge transfer transitions (ICT) (18–20). In other words, structural modification of the donor and acceptor groups attached to the molecular structure that allows charge separation in these compounds enables photophysical properties such as fluorescence spectral position, quantum yield, and lifetime to be tuned. This makes these materials valuable for applications such as organic photovoltaics (21), organic light emitting diodes (22,23), polarity or viscosity sensitive sensors (24,25) and chemosensors (26).

One of the most studied D- π -A organic systems in the literature is oxadiazole-based compounds whose photophysical properties can be adjusted with the electron-donating and -withdrawing groups. 1,3,4-oxadiazoles, the most famous

of this heterocyclic oxadiazole family consisting of two nitrogen, one oxygen, and two carbon atoms in different combinations, possess excellent electron transport functionality that enhances the fluorescence properties of the group to which they are attached. Their wide band gap and thermal stability make them an important material for organic-based optoelectronic applications with high electron mobility (27). However, 1,2,4-oxadiazoles, a member of this family, have made a name for themselves in the literature with their pharmacological properties(28). On the other hand, there are a limited number of studies in the literature on the photophysical properties of this isomer of the oxadiazole family (29–33). In these studies, it has been reported that the fluorescence emission between 360 and 500 nm in solvent upon the binding of molecules such as alkoxy, benzyl, electron-accepting carbazole, and coumarin on the 1,2,4-oxadiazole ring.

In addition, pyrazoline derivatives, just like 1,2,4-oxadiazole derivatives, have become one of the most studied molecules in the literature in recent years due to the bioactivity properties they exhibit (34–39). However, the electron-rich pyrazole ring can also act as an electron-donating (D) or electron-withdrawing (A) functional molecule due to its nitrogen (N) atoms, good electron release, high hole transfer efficiency, and some photoelectron properties (40). In addition, pyrazoline derivatives are an excellent source of blue emission as well as having excellent hole transfer performance (41,42). Therefore, pyrazoline derivatives have been widely used as hole transport materials in the fields of electrophotography and electroluminescence.

1.1 Light Generation in Lighting Technologies

Light, a fundamental and universal phenomenon, is central to our understanding of the natural world and plays a crucial role in technology, science, and daily life. Light generation is a complex process rooted in the interaction of matter and energy, and it has been a subject of study and innovation for centuries. Understanding the basic principles of light generation is essential for various scientific, technological, and practical applications, from lighting design optics to

photonics and electronics, telecommunications to laser technology, and quantum physics.

The light is a form of electromagnetic radiation that exhibits wave-particle duality. It can behave as a wave and a stream of particles called photons. It has several fundamental properties, including its speed in a vacuum, which is approximately 300 million meters per second. It can travel through space and various media and interact with matter, giving rise to phenomena such as reflection, refraction, dispersion, and absorption. This interaction between light and matter has always been interesting to scientists, who design systems to convert light into electrical energy and vice versa for sustainable living.

There are several basic light production mechanisms used especially in lighting technologies to continue our daily lives. Thermal radiation is one of the primary mechanisms by which light is generated, which is the emission of electromagnetic radiation by an object or substance due to its temperature. All objects with a non-zero temperature emit thermal radiation according to Planck's law, and the intensity and spectral composition of the radiation depends on the object's temperature. This phenomenon is observed in incandescent light bulbs, where a filament is heated to a high temperature by an electric current, causing it to emit visible light. The emitted light spectrum follows the blackbody radiation curve, with higher temperatures producing light of shorter wavelengths and higher intensities.

Gas discharge is another process of generating light in which an electric current is passed through a gas-filled tube, causing the gas to become excited and emit light in the visible spectrum. This phenomenon is utilized in various applications, such as neon signs, mercury vapor lamps, and metal halide lamps. Light emission in the blue-green spectral interval can be enhanced by introducing a mixture of neon, nitrogen, and mercury dichloride vapor.

Luminescence, another essential principle behind light generation, is the process of light emission resulting from various excitation processes (43). It can be achieved by passing an electric current through the material or exposing it to ultraviolet light. When a luminescent material is stimulated, it generally emits light

in the visible spectrum. This principle is utilized in fluorescent lamps, in which material absorbs photons of a specific wavelength and promptly emits light at a longer wavelength. Another basic light production technique that can be mentioned under luminescence phenomenon is electroluminescence. Electroluminescence is a process with the transition of the electrically pumped electrons in a material from higher to lower energy states, where a direct conversion of electric energy into visible light takes place without the generation of heat. This mechanism is at the core of light-emitting diodes (LEDs) and organic light-emitting diodes (OLEDs).

1.2 Light-Emitting Diodes (LEDs)

Light-emitting diodes (LEDs), which represent a unique combination of semiconductor physics and material engineering, have become crucial elements in the field of optoelectronics (44,45). The electroluminescence phenomenon, which is the emission of light as a result of the recombination of charge carriers (i.e., electrons and holes) within a semiconductor material, is the basis for the working principle of LEDs. This recombination process gives rise to the release of energy in the form of photons, which is determined by the bandgap of the semiconductor. The wavelength of the emitted photons (i.e., the color of the light) is directly associated with this bandgap. It can be finely tuned from the visible to the ultraviolet and infrared regions of the electromagnetic spectrum via bandgap engineering enabling by adjusting the composition of the semiconductor (46).

LED technology has offered a revolutionary advance in the field of optoelectronics used in our daily lives, such as display technologies and solid-state lighting. Here, the main advantage of LEDs compared with traditional incandescent and fluorescent lighting sources is their superior energy efficiency and durability, as well as the wide range of fine-tuned color options, making them crucial for a variety of lighting needs. However, generating white light, which is important for indoor and outdoor lighting in our daily lives, has not been achieved with a single LED chip up to now. Therefore, continuous research and innovations in the

materials and techniques that can be utilized in LED design pave the way for further improvement of their performance and energy-efficient lighting systems.

1.2.1 White Light Generation in LEDs

White light generation is a fundamental principle in lighting technology that involves the creation of light that appears white to the human eye. White light is a mixture of different wavelengths within the visible spectrum, and understanding the principles behind its generation is crucial in various lighting applications.

There are several fundamental principles and methods employed to generate white light. Color mixing and color conversion processes are the main mechanisms to achieve white light output. Color mixing involves combining different colored lights to create white light. Color conversion processes involve converting the wavelength of light using various materials (i.e., phosphors, quantum dots, and other luminescent materials) or techniques to achieve white light. Both principles rely on different mechanisms to achieve the desired white light output (45).

Color mixing is one of the fundamental principles used to generate white light. It involves combining light emissions from multiple primary colors in appropriate proportions to create a blended light that appears white. This principle is commonly used in additive color mixing systems, such as multichip RGB (red, green, blue) LEDs or mixing different color filters in traditional lighting sources. Multichip LEDs utilize chip set having different colors, such as blue, green, and red, so-called RGB-LEDs or White-LEDs (see Figure 1.1a). In this method, a high-quality white light output can be achieved by combining the emissions from different-colored LED chips. Multiple LED chips enable better control over the color temperature and color rendering index of the light produced. Additionally, multichip white LEDs offer flexibility in adjusting the intensity of each color component, allowing for customizable lighting solutions (44).

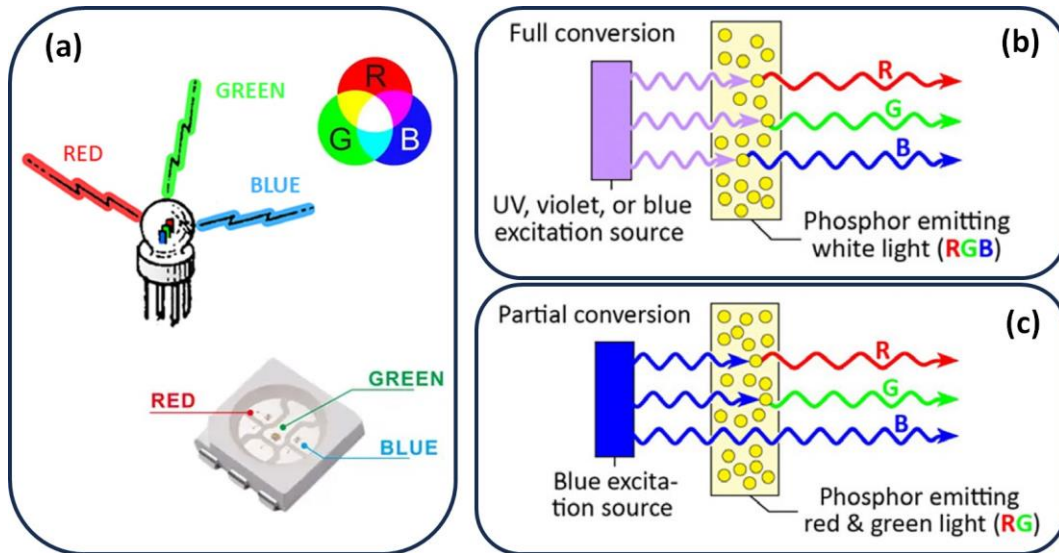


Figure 1.1. (a) White light generation with color mixing method using multichip LED. White light generation using (b) full conversion and (c) partial conversion in LEDs. This figure was adapted from (45).

Color-conversion is another widely used technique for white light generation, particularly in LED technology. In this method, specific materials, such as inorganic phosphors, quantum dots or other luminescent materials, are utilized to convert the wavelength of light emitted by primary LED chips. The LEDs using this technique are called as color-converted or phosphor-converted LEDs (47,48). This technique involves using a blue or UV LED chip as the primary light source and applying a luminescent materials coating on the chip (see Figures 1.1b and 1.1c). As the blue or UV light emitted by the LED chip interacts with the color-conversion material, a process called down-conversion occurs. Here, the color-conversion materials absorb the primary light and re-emit it as a longer wavelength, typically in the yellow to red range. Combining the blue or UV light and the re-emitted longer-wavelength light results in a mixture that appears as white light (44,45,47,48). In addition, by carefully selecting the color-conversion materials and controlling their properties, it is possible to achieve precise control over the color characteristics of the generated white light (49).

on the color aspect. The resulting x and y values represent the proportions of the three primary colors (red, green, and blue) needed to produce a specific color.

1.3.2 Correlated Color Temperature (CCT)

Another basic concept in the fields of color science and lighting technology is the correlated color temperature (CCT), and it is the most widely used metric to describe the color appearance of light sources, particularly white light sources. This metric is based on the idea that the color of a light source may be roughly compared to the color of a blackbody radiator at a certain temperature. In other words, it is a quantitative measurement of the perceived "warmth" or "coolness" of light, and it also allows for controlling and characterizing artificial light sources. The lower CCT values (e.g., 2700 K) correspond to warmer, reddish light, while the higher ones (e.g., 6500 K) represent cooler, bluish light (see Figure 1.3). For instance, the CCT value of an incandescent light bulb is below 3000K, whereas it varies between 3000 and 6500 K for fluorescent bulbs. In addition, the CCT value of the sun is nearly 6000 K (10).

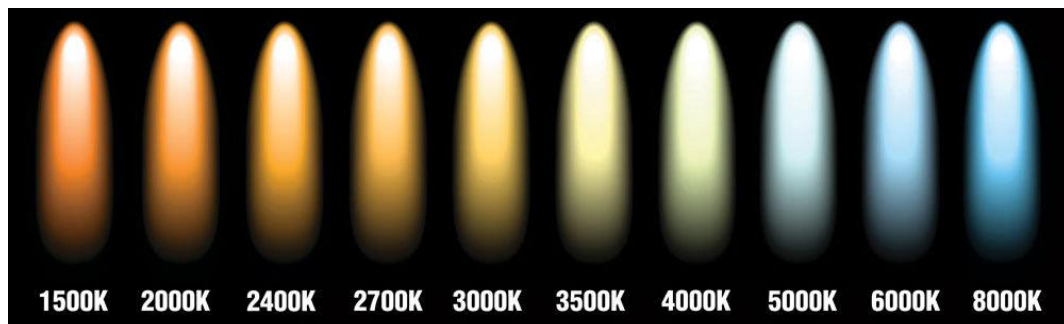


Figure 1.3. An appearance of the color of the light emitted by a light source at different correlated color temperatures (52).

1.3.3 Color Rendering Index (CRI) and Color Quality Scale (CQS)

Color Rendering Index (CRI) is a critical metric in the fields of lighting design and color science, which is developed by CIE (53,54). It is used to assess how accurately a light source reproduces the colors of objects compared to a

reference light source, typically natural daylight, or a blackbody radiator. This metric, expressed as a numerical value on a scale from 0 to 100, provides a standard for evaluating the color quality and fidelity of light sources, particularly in applications where accurate color perception is crucial, such as in photography, design, and healthcare. For example, a high CRI indicates better color rendering performance, which is capable of revealing a broader and more accurate spectrum of colors in illuminated objects (see Figure 1.4a).

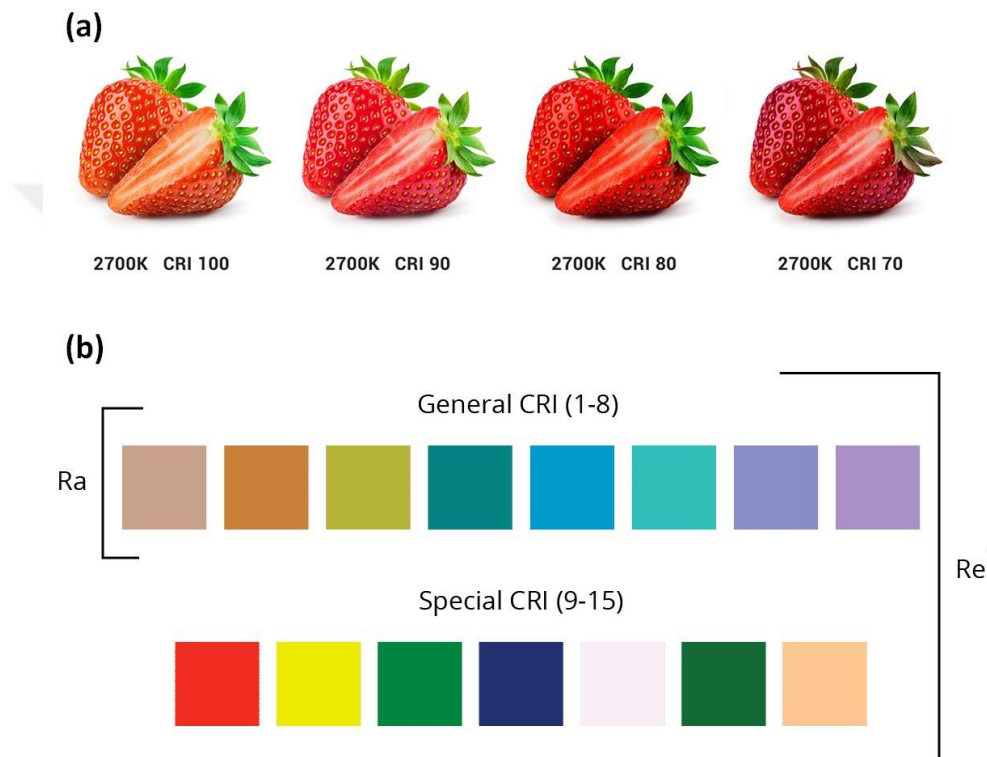


Figure 1.4. (a) Color quality and appearance under lighting containing different CRI values at 2700 K correlated color temperature (55). (b) The CRI test color samples (56).

There are eight distinct color samples, referred to as the CRI R1-R8 color samples, used in the CRI metric's evaluation of color rendering. These samples represent a range of mid-saturated and pastel colors and are used to compute the CIE General CRI value. On the other hand, the remaining samples (i.e., R9–R15), which are more saturated, are for getting exact information about the CIE Special CRI value (see Figure 1.4b). Here, the color rendering performance of a light source is determined by how well it reproduces the colors of these samples, with individual

scores assigned to each sample. Then, to provide an overall CRI value, the average CRI score is determined. If the CRI is 80 or above, it is generally considered good. The higher scores indicate the better color rendering capabilities of the light source.

The Color Quality Scale (CQS) is a new and alternative metric providing a quantitative evaluation of how accurately a light source reproduces colors compared to a reference illuminant (57). It has been developed as an enhanced version of the traditional CRI metric by the National Institute of Standards and Technology (NIST) and overcomes the limitations of the CRI by offering a more accurate and comprehensive assessment of color quality. Here, a score is assigned to a light source based on its ability to render fifteen commercially available Munsell color samples, accounting for both fidelity (i.e., the degree to which the colors correspond to those in a reference source) and gamut (i.e., how broad a range of colors can be accurately rendered). The score is expressed numerically between 0 and 100. The high CQS scores correspond to better color quality. In other words, a light source with a CQS score of 100 accurately reproduces colors similar to the reference illuminant, while lower ones indicate a deviation in color rendering.

1.4 Principles of Absorption and Fluorescence

The absorption of light is a fundamental optical phenomenon that is essential to many different scientific fields and applications. In this physical process, as a photon interacts with a material, its energy is transferred to the matter. In other words, the energy of the photon is absorbed by the material. Briefly, if the frequency of the incident wave, typically in the visible or ultraviolet region of the electromagnetic spectrum, is at or near the vibration frequency of the electrons of the atoms forming the matter, the absorbed energy is transformed by the electrons into vibrational motion. This leads to a change in the energy state of the electrons from the ground state to the excited state. Here, both the ground and excited states are called as singlet state where the intrinsic angular momentum (i.e., spin) of the pair of electrons is in the antisymmetric configuration, i.e., the total spin of electrons is zero (58). In the frame of an organic compound, this process occurs as the electrons in the bonding and/or nonbonding orbitals are promoted to the empty antibonding orbitals by the absorbed energy of the incident wave. There is a direct

relationship between the energy gap and the energy (i.e., wavelength) of the absorbed photon. For instance, to promote a transition to higher states, it needs high energy (i.e., a short wavelength). In the UV-Vis region of the electromagnetic spectrum (i.e., in the range of 200–800 nm), there are three important transitions between the orbitals: pi-bonding and pi-antibonding orbitals ($\pi \rightarrow \pi^*$), nonbonding and pi-antibonding orbitals ($n \rightarrow \pi^*$), and nonbonding and sigma-antibonding orbitals ($n \rightarrow \sigma^*$) (see Figure 1.5a). The other transitions (i.e., from sigma-bonding to pi-antibonding orbitals ($\sigma \rightarrow \pi^*$) or from sigma-bonding to sigma-antibonding orbitals ($\sigma \rightarrow \sigma^*$)) are generated by absorbing the photons having a wavelength less than 200 nm. In other words, if a molecule has pi-bonds or atoms contain nonbonding orbitals (e.g., oxygen, nitrogen, or halogen atoms comprising a lone pair), these transitions can be observed in the UV-Vis region (59).

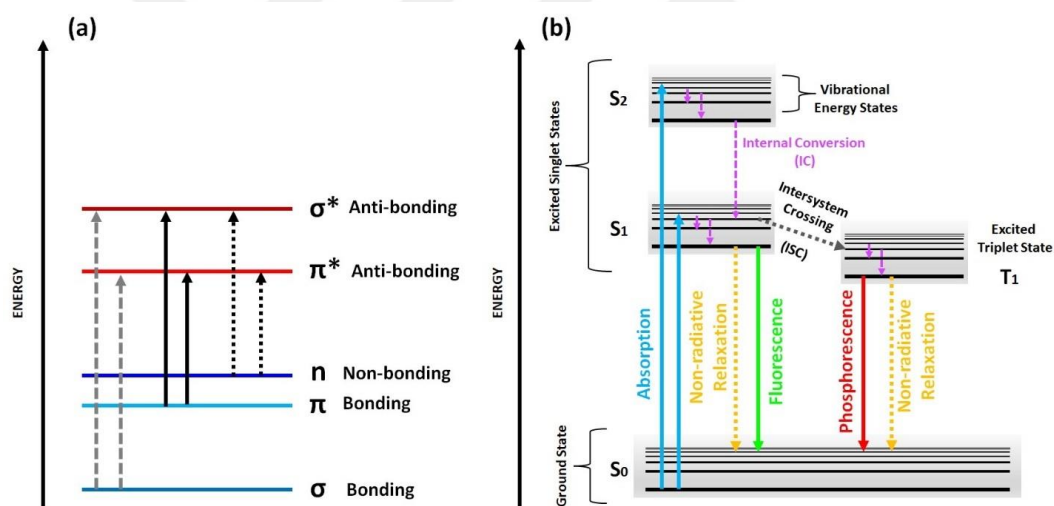


Figure 1.5. (a) Absorption process in molecular state. The solid, dashed, and dotted lines represent the transitions between molecular orbitals. (b) Jablonski diagram for absorption, fluorescence, and phosphorescence phenomena between electronic states (58,59).

On the other hand, fluorescence is another optical phenomenon resulting in the emission of a photon following absorption (see Figure 1.5b). Briefly, the excited molecule absorbing a photon having sufficient energy can then undergo radiative decay, emitting lower energy (longer wavelength) photon than the incident photon, which is known as the Stokes shift. After this fluorescence phenomenon that occurs

in the time scale of picoseconds to nanoseconds, the molecule returns to its original position, i.e., ground state. Furthermore, the excited molecule can also undergo non-radiative relaxation, losing energy through vibrational relaxation (i.e., internal conversion and intersystem crossing). If these non-radiative decay processes take place on a time scale comparable to a molecule's average time being in the excited state before emitting a photon (i.e., fluorescence lifetime), they can always compete with the radiative decay ones. This competition also directly affects the efficiency of the fluorescence process, i.e., the ratio of the photons emitted to the photons absorbed by the molecule, which is called the quantum yield. These characteristics (i.e., spectral position, fluorescence quantum yield, and lifetime) can also be affected by the close interaction of the excited molecule with the microenvironment, due to possible changes in the radiative and non-radiative processes (58). Therefore, changes in characteristics can also provide information about the microenvironment surrounding the fluorescent molecule. Moreover, some physical and chemical parameters such as temperature, pressure, viscosity, electrical potential, polarity, pH, quenchers, ions, and hydrogen bonds that characterize the microenvironment can also affect the characteristics of the fluorescence molecule (59).

1.5 Organic Fluorescent Materials

Fluorescent materials, including both inorganic and organic compounds, are one of the significant and dynamic areas of research and application within the field of materials science. Inorganic fluorescent materials are commonly based on semiconductors or metal complexes with their high quantum yields and photostability. For instance, semiconductor quantum dots (e.g., CdSe, CdTe, ZnS, etc.) have superior optical properties, which can be fine-tuned by changing their size in nanoscale, enabling advantageous for biological and optoelectronic applications (60–67). On the other hand, compared to inorganic ones, organic fluorescent materials are nontoxic and simpler to synthesize (68,69). This material group includes a broad spectrum of compounds and polymers exhibiting unique photophysical properties, that can be precisely engineered making them

indispensable in fields such as fluorescence microscopy, organic light-emitting diodes (OLEDs), and sensing technologies. The emission kinetics of these materials depend on structural design strategies allowing relevant electronic transitions. In the case of conventional organic molecules (e.g., rhodamine, fluorescein, and BODIPY) and polymers, the emission kinetic is associated with the movement of charge carriers (i.e., electrons and holes) along the entire structure. On the other hand, in the case of organic compounds comprising electron-donating (donor, D) and electron-withdrawing (acceptor, A) groups, the emission kinetic is generally governed by intramolecular charge transfer transitions (ICT) (70–73). In other words, the modification of the molecular structure with the donor and acceptor groups enables a charge separation on the structure of the target molecule, which can result in dramatic changes in the photophysical properties such as fluorescence spectral position, quantum yield, and lifetime.

Organic fluorescence materials generally suffer from an aggregated or closely packed state, even though they display well fluorescence properties in their dilute solutions. In the case of transition from solution to solid phase (i.e., crystals and thin films), it is observed that a reduction or complete disappearance in their fluorescence intensity owing to the aggregation in molecular state, which is called Aggregation-Caused Quenching (ACQ) (73,74). This phenomenon is generally attributed to intermolecular interactions, such as pi-pi stacking promoting the nonradiative recombination pathways, that occur in the aggregation state (70,71). The disappearance or decrease in emission significantly limits the usage of the organic compounds in applications needing efficient fluorescence properties in concentrated solutions or solid-state (75–78). Therefore, in the literature, there are numerous studies on developing organic materials that exhibit solid-state emission via reducing or suppressing the ACQ effect (79–81). For instance, in the early 2000s, a group of researchers reported an unusual phenomenon called aggregation-induced emission (AIE) (72,82–85). In these studies, while the molecules exhibited fluorescence emission in the solid state, no emission was detected in their solution phase. This phenomenon is generally attributed to the restriction of intramolecular motions (RIM) (i.e., intramolecular rotations and vibrations) in the solid phase to the solution one (85). On the other hand, in recent years, it has been reported that some

organic molecules have exhibited fluorescence properties both in their solid and solution phases (86–90). For instance, it was reported that a series of conjugated molecules (i.e., triazolopyridine-thiophene) in the donor-acceptor-donor (D-A-D) structure exhibited fluorescence emission with a quantum yield of 89% in solution and 29% in solid phases (89).

1.6 Pyrazolines

1.6.1 Chemical Structure and Properties of Pyrazolines

Pyrazoline is a heterocyclic compound with a five-membered ring containing three C, two N atoms and a double bond. General chemical formula is given as $C_3H_4N_2$, but its derivatives can have various substituents attached to the ring, such as alkyl, aryl, halogen, or other functional groups. These substituents contribute to the unique properties of different pyrazoline derivatives (91).

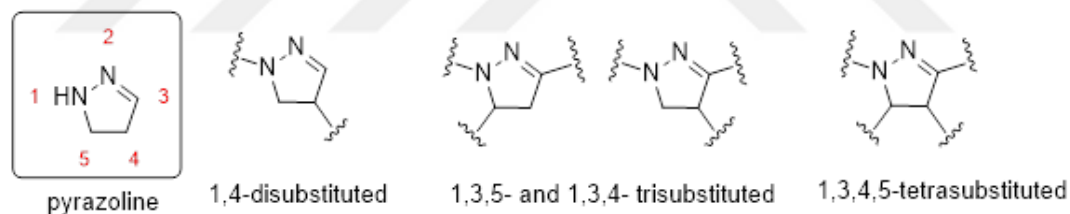


Figure 1.6. General structure of pyrazoline and substituted pyrazolines.

Pyrazolines are generally stable compounds, especially compared to other reactive heterocycles resistant to decomposition under normal conditions. However, their strength can be influenced by the nature and position of substituents and environmental factors. They can withstand a range of reaction conditions and have good thermal stability (92).

The solubility of pyrazolines can vary depending on their molecular structure and the nature of substituents. Hydrophilic groups can enhance solubility in water, while hydrophobic groups can increase solubility in organic solvents.

Most of its derivatives are soluble in common organic solvents, while others may require specific solvents or conditions for dissolution (93).

Pyrazoline derivatives are versatile building blocks for the synthesis of complex organic compounds due to their ability to undergo various chemical reactions such as nucleophilic substitution, oxidation, reduction, and cyclization reactions. These reactions allow the synthesis of diverse pyrazoline-based compounds with tailored properties (94).

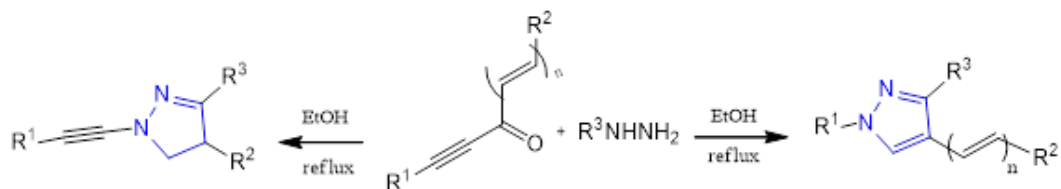
Chemical structure and properties of pyrazolines make it a versatile scaffold for developing various functional compounds (95). The ability to modify the substituents on the pyrazoline ring allows for fine-tuning its chemical and biological properties (96). This versatility provides for the development of compounds with optimized properties for specific applications, making pyrazoline chemistry an active area of research and exploration (94).

Pyrazoline derivatives exhibit interesting optical properties, including absorption in UV-Vis region, making them suitable for applications such as dyes, pigments, fluorescence probes, sensors, and optoelectronic devices. The absorption wavelength can be influenced by the nature and position of substituents on the pyrazoline ring. For example, in the study of Uchacz et al. and photophysical properties of some pyrazolines were investigated and it showed that the pyrazoline-based probes can detect sulphite anions with high selectivity and sensitivity (97). These findings highlight the potential of pyrazoline derivatives for various applications in the field of optics and photonics.

1.6.2 Synthesis of Pyrazolines

When synthesis of pyrazoline derivatives have been explored, it will be seen that many research studies on pyrazoline compounds highlights their importance in heterocyclic chemistry and their potential for various biomedical and materials science applications. There are several methods available for the preparation of pyrazolines, each with its advantages and limitations. Some commonly used synthetic methods are presented below (94,98–101).

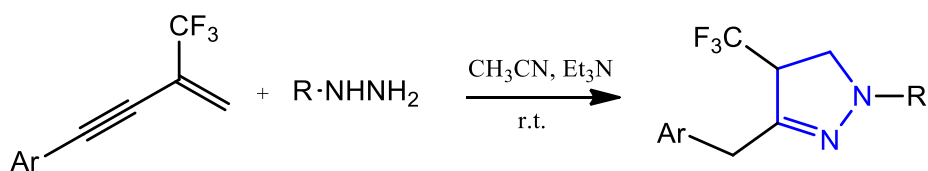
Pyrazoles and pyrazolines can be synthesized via cyclocondensation of α,β -unsaturated carbonyl compounds with hydrazine derivatives (102).



Scheme 1.1. Synthesis of alkynylpyrazolines and alkenylpyrazoles.

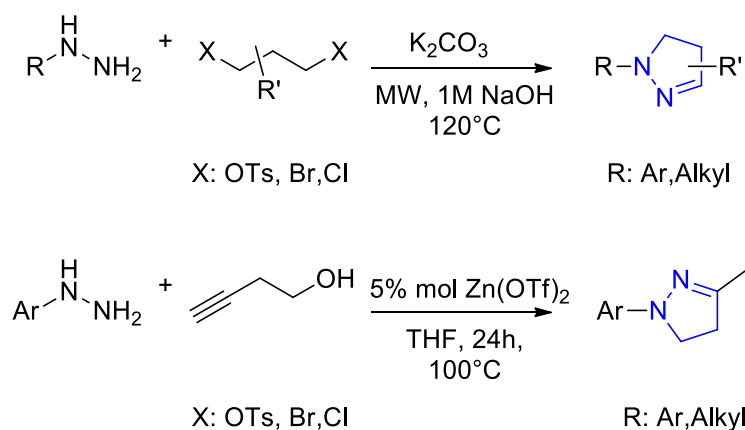
The reactions of hydrazines with α,β -unsaturated carbonyl compounds has also been investigated, leading to the formation of 2-pyrazolines, with the structure of some products determined through theoretical calculations and NMR spectroscopy (103).

In addition, the reaction of β -trifluoromethyl-1,3-enyne with hydrazines can lead to the synthesis of trifluoromethylation pyrazolines (104).



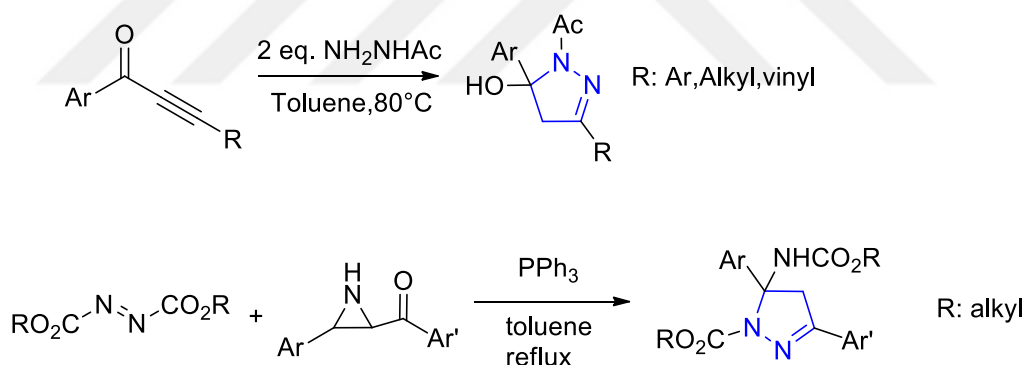
Scheme 1.2. Synthesis of trifluoromethylpyrazolines.

One-pot synthesis of pyrazolines from alkyldihalides and hydrazines occurs under microwave irradiation via a simple and efficient cyclocondensation in an alkaline aqueous medium (105). Also, arylhydrazines regioselectively react with 3-butynol in the presence of a catalytic amount of zinc triflate to give aryl-substituted pyrazolines (106).



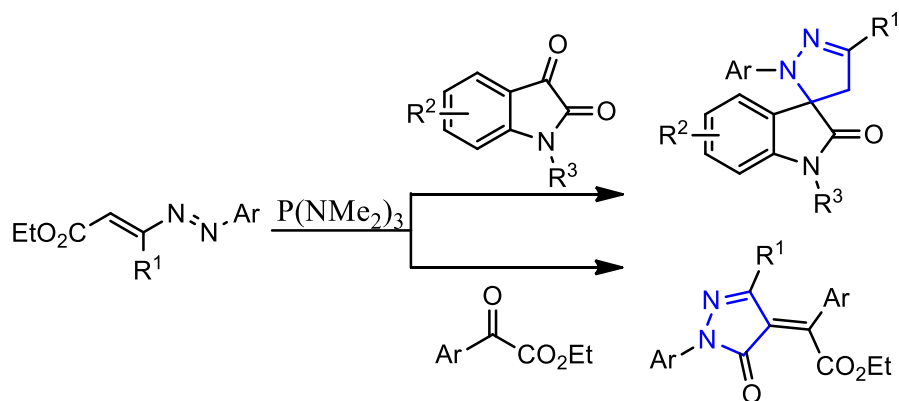
Scheme 1.3. One-pot synthesis of pyrazoline derivatives using hydrazines.

Various 1-acyl-5-hydroxy-4,5-dihydro-1H-pyrazoles have been prepared in good yields from the corresponding 2-alkyn-1-ones (107). A novel, efficient, and general domino reaction of 2-acylaziridines with the Huisgen zwitterions furnishes pyrazolines (108).



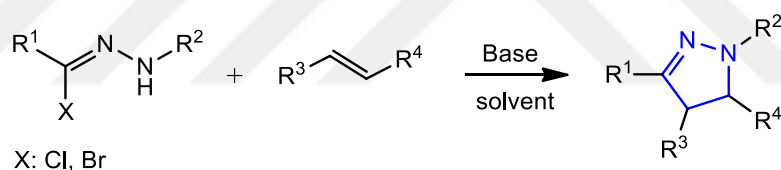
Scheme 1.4. Synthesis of 4-pyrazolines using alkyn-1-ones and acylaziridines.

The synthesis of pyrazolines can also be done by annulation of azoalkenes with α -dicarbonyl compounds using $\text{P}(\text{NMe}_2)_3$ as a mediator (109).



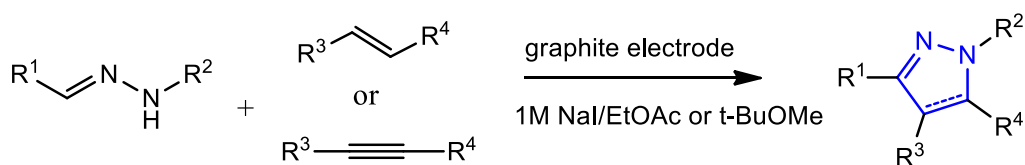
Scheme 1.5. Synthesis of spirooxindole-pyrazolines and pyrazolones

The synthesis of pyrazolines via cycloaddition reactions of hydrazones or hydrazonyl halides with variety of alkene dipolarophiles has been extensively studied applying various strategies (110).



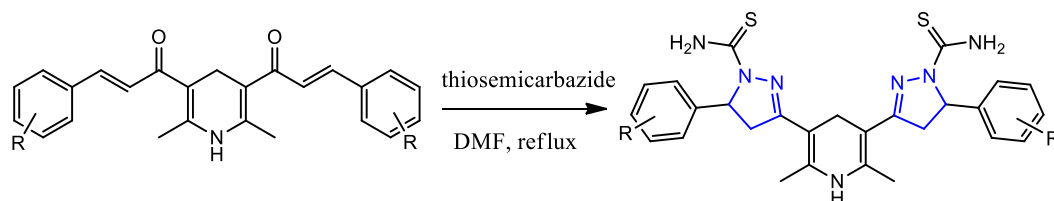
Scheme 1.6. Synthesis of pyrazolines via nitrilimine cycloadditions.

Additionally, an electrochemical approach has been used to directly synthesize pyrazolines and pyrazoles from hydrazones and dipolarophiles, using a biphasic system and sodium iodide as a mediator (111).



Scheme 1.7. Synthesis of pyrazolines using electrochemical method

Another method involved the condensation of 2,6-dimethyl-3,5-diacetyl-1,4-dihydropyridine with benzaldehydes, followed by the synthesis of bis- α,β -unsaturated carbonyl compounds, which can serve as intermediates for the formation of bis-pyrazolines (100).



Scheme 1.8. Synthesis of bis-pyrazolines using thiosemicarbazide.

In summary, these methods provide efficient routes to synthesize pyrazolines from readily available starting materials and offer good yields and diverse substitution patterns. The specific method employed depends on the starting materials and desired structural features. Besides, pyrazolines can undergo further modifications to introduce additional functional groups or structural variations via oxidation, reduction, acylation, or substitution reactions (112).

1.6.3 Applications of Pyrazolines in Material Science

Pyrazolines have diverse applications in material science due to their unique chemical and physical properties. They can serve as building blocks for synthesizing novel materials, such as OLEDs, fluorescent probes, semiconductors, and polymers. Researchers have achieved materials with enhanced thermal stability, optical properties, and electrical conductivity by incorporating pyrazoline moieties into their structures (113). Therefore, using pyrazoline compounds in material science holds promise for developing novel materials with enhanced properties.

Pyrazoline-based fluorescent imaging probes have been designed and synthesized in several studies. For instance, some new pyrazoline derivatives were designed as fluorescent probes for the fluorometric detection of Cu^{2+} ions with high selectivity and resistance to perturbations (114). Besides, two pyrazoline-based fluorescent and colorimetric probes for detection of sulfite ion were prepared and their photophysical properties have been studied recently (97). Rangasamy and Palaninathan designed pyrene-appended pyrazoline compounds, with one of them displaying excellent selectivity and sensitivity to Al^{3+} ions (115).

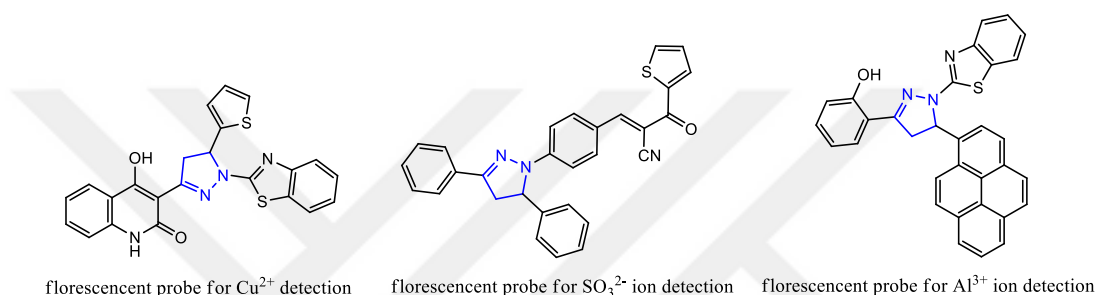


Figure 1.7. Pyrazoline-based fluorescent probes for ion detection.

Furthermore, several studies have focused on synthesizing and characterizing pyrazoline-derived ligands and their complex compounds with metal ions. Pyrazoline derivatives have been widely used as chemosensors for the selective detection of heavy metal ions, specifically Hg^{2+} and Cd^{2+} (116). Fluorescence studies have shown that the metal ion complex compounds with pyrazoline-derived ligands can detect heavy metal ions Hg^{2+} and Cd^{2+} with a turn-on or turn-off response. These derivatives have photophysical properties and can chelate metal ions, resulting in strong absorption, emission, and fluorescence properties (117,118). These findings demonstrate the potential of pyrazoline derivatives as selective chemosensors for detecting heavy metal ions.

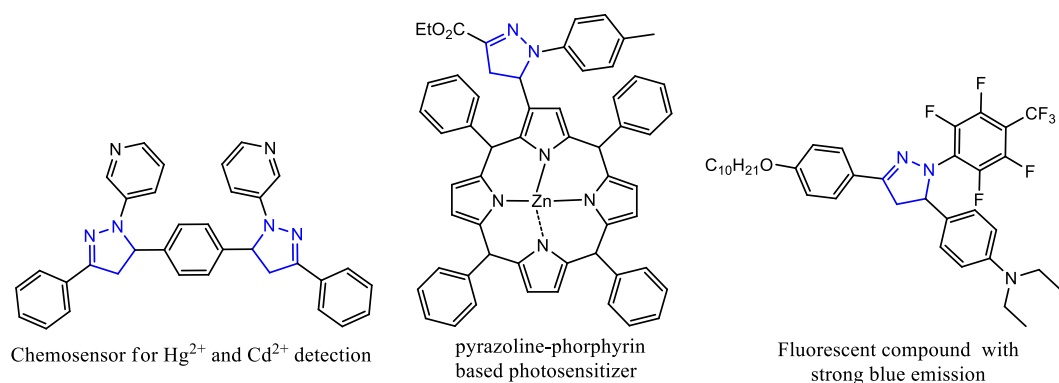


Figure 1.8. Pyrazoline-based fluorescent chemosensors for heavy metals.

Pyrazoline-based materials have shown potential for sensing environmental pollutants. Novel nine coumarin-based pyrazolines have been synthesized and characterized as highly fluorescent materials, exhibiting stimuli-responsive chromic behaviors such as thermo-, mechano-, solvato-, vapochromic, and ionochromic properties (119). A pyrazoline derivative has been identified as a fluorescence chloride sensor, capable of detecting multiple halides and behaving differently depending on the nature of the halide or metal counterion (120). Another pyrazoline derivative has been used for metal ion selectivity, specifically detecting Hg^{2+} ions with high binding constant and selectivity (121).

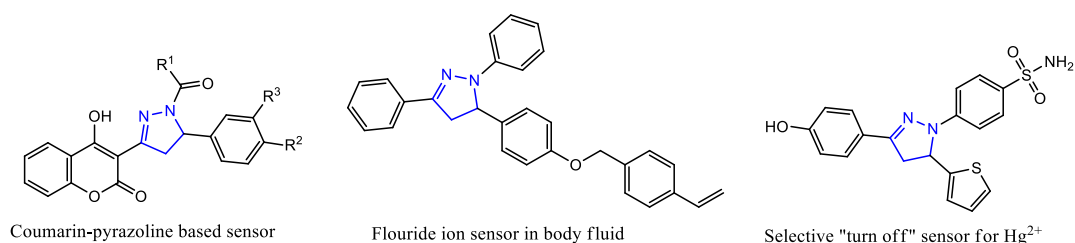


Figure 1.9. Pyrazoline-based fluorescent sensors for environmental samples.

On the other hand, the research and development of pyrazoline-based materials can provide new insights and possibilities for the future of OLED technology. A few recent studies on the synthesis of pyrazoline-based luminescent materials can be given as below. For instance, two thiophene or furan decorated pyrazoline-based fluorescent compounds were synthesized, characterized and their

thermal stabilities, emission properties, quantum yields, lifetimes and semiconductor properties were investigated (122). Thiophene and furan containing pyrazoline luminescent materials for optoelectronics. In another recent study, highly luminescent thiophene, furan, pyridine substituted pyrazolines have been prepared and studied for their theoretical and experimental properties (123). Recently, some pyrene-pyrazolines have been synthesized, which exhibit green and yellow emissions in solid state (124).

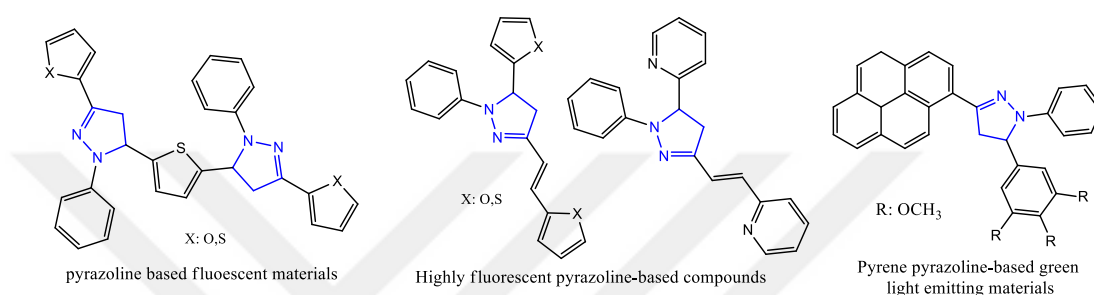


Figure 1.10. Pyrazoline-based highly fluorescent OLED materials.

In addition, some pyrazoline derivatives exhibit photochromic properties, meaning their color or optical properties can change upon exposure to light. These materials have potential applications in optical switches, data storage devices, and optical memory systems. For example, Feng et al. synthesized two novel 1,3,5-trisubstituted pyrazoline derivatives and investigated their optical properties (125). Mysliwiec et al. reported on the synthesis and optical properties of pyrazoline derivatives that exhibited efficient broadband photoluminescence, making them suitable for lasing applications (126). Gong et al. synthesized a series of pyrazoline derivatives and investigated their absorption and fluorescence spectral characteristics, showing potential for applications in optical devices (127).

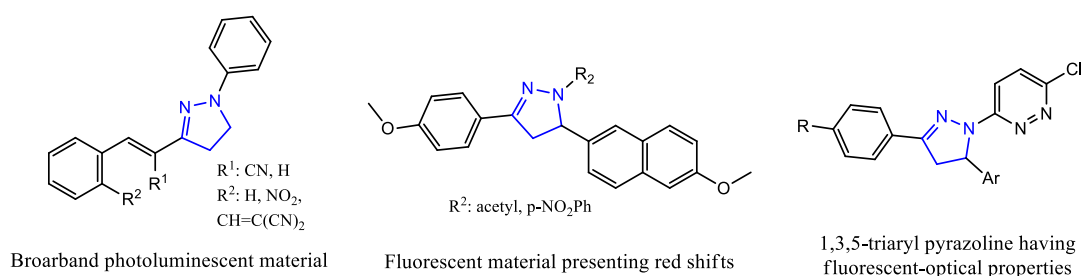


Figure 1.11. Di- and tri-substituted pyrazolines with optical and luminescent properties.

2. AIM AND SCOPE OF THE STUDY

The need for energy to meet the needs of daily life is also increasing with the increasing human population year by year. One of the elements that contribute significantly to global energy consumption due to the increasing human population is artificial lighting applications, which are indispensable for today's modern social life and one of the largest areas of electricity usage in the world. Solid-state lighting (SSL) technology, which consists of light-emitting diodes (LED), appears as an alternative to incandescent lamps, which are very poor in terms of energy efficiency, and fluorescent lamps, which have reached saturation in terms of efficiency. For this reason, research on methods and materials that will increase both energy and lighting efficiency in LED technology and applications has accelerated in recent years. When rare-earth ion-doped phosphors such as gadolinium, cerium, and terbium, which are used in phosphor-converted LEDs based on the principle of obtaining white light by color conversion with high-energy photons in both industry and academic research, are evaluated in terms of cost and raw material accessibility, there is a need for research and development of new and efficient fluorescent materials in this field. An important alternative as a color conversion material is fluorescent organic compounds owing to their advantages such as photophysical properties, easy synthesis, low cost, and low toxicity.

To this end, in this study, pyrazoline derivatives functionalized with 1,2,4-oxazidazole ring, which have fluorescence properties both in solution and solid-state, were synthesized by nitrilimine cycloaddition enabling a simple and flexible way for attachment or modification of substituted aryl groups on the main skeleton. Depending on the attachment positions and electron-donating or withdrawing abilities of the substituent groups on the main skeleton, the photophysical properties of the compounds both in the solution and solid-state are going to be investigated. In the case of the solution phase, it is also aimed to investigate the effect of the polarity of the medium surrounding the compounds (i.e., solvent) on the photophysical properties. Furthermore, as a proof-of-concept demonstration, after the determination of their photophysical properties in their solid-state phase, it is purposed to investigate and analyze the potentials of the synthesized compounds as color converter materials for color-conversion LED applications.

3. MATERIALS AND METHODS

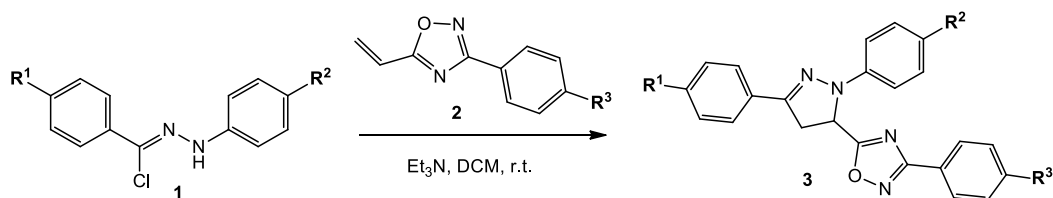
3.1 Chemicals and Instruments

All the reagents and solvents were purchased from commercial sources and utilized without any additional purification. Standard techniques were used to dry the solvents. Thin layer chromatography (TLC) was used to keep track of the reactions. The chromatograms were seen using UV light and KMnO₄. IR spectra were recorded on a Shimadzu FT-IR-8400S instrument (KBr pellet or NaCl discs) and a Shimadzu FT-IR Spectrometer with an ATR system. ¹H- and ¹³C- NMR spectra were recorded on VARIAN spectrometers (400 MHz for proton and 100 MHz for carbon) spectrometer at ambient temperature. All NMR spectra were obtained in CDCl₃ or DMSO-d₆ using Me₄Si as an internal standard at 400 MHz for proton and 100 MHz for carbon-13, respectively. The following acronyms are used to describe peak multiplicities: s stands for singlet; d stands for doublet; q stands for a quartet. On Merck silica gel F254 plates, analytical TLC was performed. Ethyl acetate/n-hexane were employed as eluents in flash chromatographic purifications using Merck Silica gel 60 (230–400 mesh ASTM) as the stationary phase. Melting points (mp) were determined using a MELTEMP instrument in open capillary tubes and are uncorrected.

3.2 Experimental

3.2.1 Synthesis of 1,3-diarylsubstituted-5-(1,2,4-oxadiazolyl)pyrazolines (3)

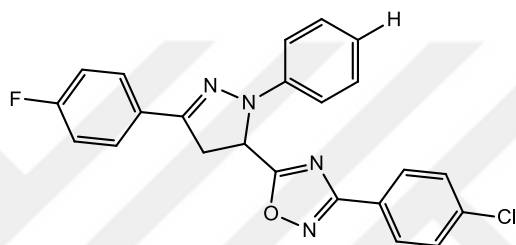
General Method



To a solution of hydrazone chloride **1** (0.3 mmol, 1.0 eq.) and 3-aryl-5-vinyl-1,2,4-oxadiazole **2** (0.3 mmol, 1.0 eq.) in dry DCM (10 mL) at ambient temperature, Et₃N (3.74 g, 1.2 mmol, 4.0 eq.) was added dropwise. The resulting mixture was stirred at room temperature until consumption of starting compounds and reaction

progress was checked by using TLC analysis. Upon completion of reaction, reaction mixture was mixed with water (10 mL) and extracted with DCM (3x10mL). The organic phases were collected and dried over Na₂SO₄ and then, filtered. Finally, DCM was evaporated under vacuum to afford crude 1,3-diarylsubstituted-5-(1,2,4-oxadiazolyl)pyrazolines **3** which was then purified and isolated using column chromatography.

3-(4-chlorophenyl)-5-(3-(4-fluorophenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-5-yl)-1,2,4-oxadiazole (3a) (PyOx-1)

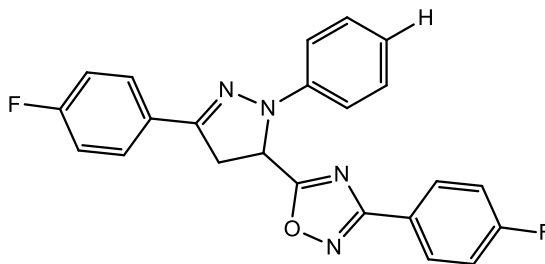


Column chromatography (11% EtOAc/hexane) afforded white crystals. Yield: (0.110 g, 88%), *R_f* (%15 EtOAc/hexane) 0.40. IR (ATR, cm⁻¹): ν = 2921-2853 (C-H), 1594 (C=N), 1553 (C=N), 1497 (C=C), 1267 (C-O), 1121, 828 (N-O), 751 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.73 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.10 (t, *J* = 8.6 Hz, 2H), 6.88 (t, *J* = 7.2 Hz, 1H), 5.62 (dd, *J* = 12.5, 6.8 Hz, 1H), 3.86 (dd, *J* = 17.0, 12.6 Hz, 1H), 3.61 (dd, *J* = 17.0, 6.8 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 178.37, 167.91, 164.62, 162.14, 146.52, 144.42, 137.70, 129.30, 128.91, 127.95, 124.75, 120.66, 115.94, 115.82, 113.65, 56.43, 39.78.

HRMS (TOF-MS APCI⁺): [M+H]⁺, found 419.1070. C₂₃H₁₇ClFN₄O requires 419.1075.

3-(4-fluorophenyl)-5-(3-(4-fluorophenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-5-yl)-1,2,4-oxadiazole (3b) (PyOx-2)



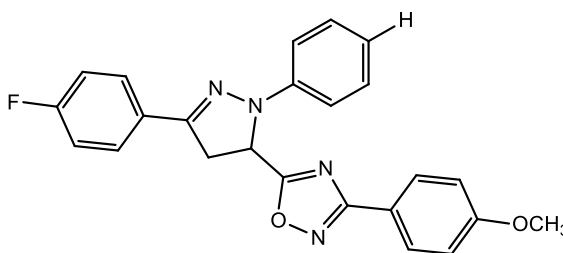
Rotary chromatography (Chromatotron) (15% EtOAc/hexane) afforded gray-white powder. Yield: (0.100 g, 83%), R_f (17% EtOAc/hexane) 0.50. IR (ATR, cm^{-1}): ν = 3006 (arom.CH), 2925-2857 (C-H), 1595 (C=N), 1556 (C=N), 1497 (C=C), 1261(C-O), 1121, 830(N-O), 750 cm^{-1} .

^1H NMR (400 MHz, CDCl_3) δ 8.06 (dd, J = 8.8, 5.4 Hz, 2H), 7.75 (dd, J = 8.7, 5.4 Hz, 2H), 7.33- 7.25 (m, 2H), 7.16 (ddd, J = 17.4, 13.2, 8.3 Hz, 5H), 6.91 (t, J = 7.2 Hz, 1H), 5.64 (dd, J = 12.5, 6.8 Hz, 1H), 3.88 (dd, J = 17.1, 12.5 Hz, 1H), 3.64 (dd, J = 17.1, 6.8 Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 178.48, 168.02, 167.73, 166.18, 164.58, 163.67, 162.11, 151.97, 144.64, 139.68, 130.04, 129.94, 129.85, 129.56, 129.42, 129.16, 128.15, 128.07, 127.97, 127.89, 126.45, 122.71, 122.68, 120.85, 116.49, 116.27, 116.20, 115.98, 113.82, 108.95, 56.64, 39.97.

HRMS (TOF-MS APCI+): $[\text{M}+\text{H}]^+$, found 403.1348. $\text{C}_{23}\text{H}_{17}\text{F}_2\text{N}_4\text{O}$ requires 403.1370.

5-(3-(4-fluorophenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-5-yl)-3-(4-methoxyphenyl)-1,2,4-oxadiazole (3c) (PyOx-3)



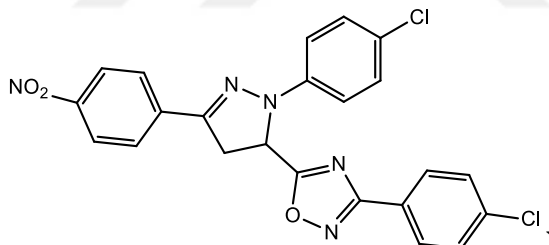
Rotary chromatography (Chromatotron) (20% EtOAc/hexane) afforded white solid. Yield: (0.100 g, 80%), R_f (%33 EtOAc/hexane) 0.75. IR (ATR, cm^{-1}): ν = 3021 (arom.CH), 2978-2851 (C-H), 1594 (C=N), 1566(C=N), 1498 (C=C), 1257(C-O), 1113, 834 (N-O), 750 cm^{-1} .

^1H NMR (400 MHz, cdcl_3) δ 8.01 (d, J = 8.8 Hz, 2H), 7.76 (dd, J = 8.7, 5.4 Hz, 2H), 7.29 (t, J = 7.8 Hz, 2H), 7.22 (d, J = 7.9 Hz, 2H), 7.13 (t, J = 8.6 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 6.91 (t, J = 7.2 Hz, 1H), 5.63 (dd, J = 12.5, 7.0 Hz, 1H), 3.87 (3H, s), 3.95 – 3.79 (m, 1H), 3.64 (dd, J = 17.1, 7.0 Hz, 1H).

^{13}C NMR (101 MHz, cdcl_3) δ 177.81, 168.36, 164.59, 162.11, 146.48, 144.50, 129.28, 129.22, 128.01, 127.93, 127.84, 120.56, 118.67, 115.94, 115.73, 114.27, 113.62, 56.51, 55.40, 39.76.

HRMS (TOF-MS APCI+): $[\text{M}+\text{H}]^+$, found 415.1562. $\text{C}_{24}\text{H}_{20}\text{FN}_4\text{O}_2$ requires 415.1570.

3-(4-chlorophenyl)-5-(1-(4-chlorophenyl)-3-(4-nitrophenyl)-4,5-dihydro-1H-pyrazol-5-yl)-1,2,4-oxadiazole (3d) (PyOx-4)



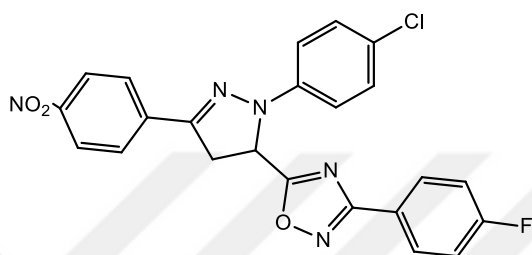
Column chromatography (50% EtOAc/hexane) afforded orange powder. Yield: (0.139 g, 96%), R_f (%33 EtOAc/hexane) 0.70. IR (ATR, cm^{-1}): ν = 2925-2846 (C-H), 1595 (C=N), 1553(C=N), 1512 (NO_2 str.), 1488 (C=C), 1325 (NO_2 str.), 1250(C-O), 1138, 846 (N-O), 751 cm^{-1} .

^1H NMR (400 MHz, cdcl_3) δ 8.29 (d, J = 8.9 Hz, 2H), 7.98 (d, J = 8.5 Hz, 2H), 7.88 (q, J = 4.9 Hz, 2H), 7.45 (d, J = 8.5 Hz, 2H), 7.29 – 7.23 (m, 2H), 7.16 (d, J = 9.0 Hz, 2H), 5.77 (dd, J = 12.7, 6.3 Hz, 1H), 3.95 (dd, J = 17.2, 12.7 Hz, 1H), 3.72 (dd, J = 17.2, 6.3 Hz, 1H).

^{13}C NMR (101 MHz, cdCl_3) δ 177.18, 167.98, 147.71, 145.25, 141.69, 137.88, 137.43, 129.32, 129.25, 128.83, 126.75, 126.48, 126.37, 124.41, 124.13, 115.01, 56.35, 39.16.

HRMS (TOF-MS ESI-): $[\text{M}]^+$, found 479.0526. $\text{C}_{23}\text{H}_{15}\text{Cl}_2\text{N}_5\text{O}_3$ requires 479.0551.

5-(1-(4-chlorophenyl)-3-(4-nitrophenyl)-4,5-dihydro-1H-pyrazol-5-yl)-3-(4-fluorophenyl)-1,2,4-oxadiazole (3e) (PyOx-5)



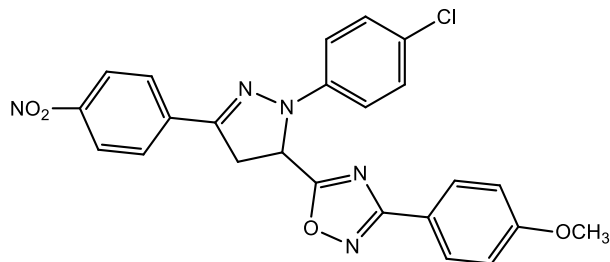
Column chromatography (20% EtOAc/hexane) afforded yellow solid. Yield: (0.110 g, 79%), R_f (%33 EtOAc/hexane) 0.80. IR (ATR, cm^{-1}): ν = 3013 (arom.CH), 2917-2850 (C-H), 1590 (C=N), 1564(C=N), 1513 (NO_2 str.), 1488 (C=C), 1350 (NO_2 str.), 1275(C-O), 1077, 812(N-O), 749 cm^{-1} .

^1H NMR (400 MHz, cdCl_3) δ 8.30 (d, J = 8.7 Hz, 2H), 8.06 (dd, J = 8.5, 5.5 Hz, 2H), 7.90 (d, J = 8.7 Hz, 2H), 7.27 (d, J = 7.4 Hz, 2H), 7.17 (t, J = 8.5 Hz, 4H), 5.78 (dd, J = 12.7, 6.3 Hz, 1H), 3.97 (dd, J = 17.2, 12.7 Hz, 1H), 3.74 (dd, J = 17.1, 6.3 Hz, 1H)

^{13}C NMR (101 MHz, cdCl_3) δ 177.50, 168.41, 166.45, 163.94, 148.03, 145.72, 142.11, 137.88, 130.14, 129.76, 126.84, 124.56, 122.58, 116.72, 116.51, 115.41, 56.76, 39.58.

HRMS (TOF-MS APCI+): $[\text{M}+\text{H}]^+$, found 464.0905. $\text{C}_{23}\text{H}_{15}\text{ClFN}_5\text{O}_3$ requires 464.0905.

5-(1-(4-chlorophenyl)-3-(4-nitrophenyl)-4,5-dihydro-1H-pyrazol-5-yl)-3-(4-methoxyphenyl)-1,2,4-oxadiazole (3f) (PyOx-6)



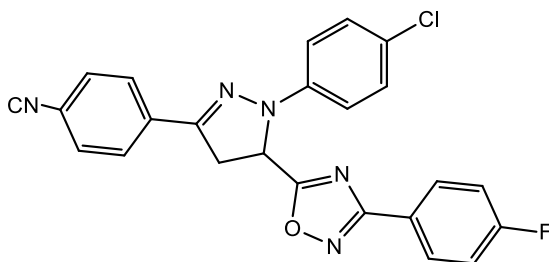
Rotary chromatography (Chromatotron) (11-33% EtOAc/hexane) afforded orange powder. Yield: (0.130 g, 91%), R_f (%33 EtOAc/hexane) 0.70. IR (ATR, cm^{-1}): ν = 3006 (arom.CH), 2981-2850 (C-H), 1593 (C=N), 1555(C=N), 1512 (NO_2 str.), 1489 (C=C), 1324 (NO_2 str.), 1259 (C-O), 1089, 846 (N-O), 749 cm^{-1} .

^1H NMR (400 MHz, cdcl_3) δ 8.29 (d, J = 8.4 Hz, 2H), 7.98 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 9.2 Hz, 2H), 7.18 (d, J = 8.6 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 5.75 (dd, J = 12.6, 6.3 Hz, 1H), 3.94 (dd, J = 17.0, 13.0 Hz, 1H), 3.88 (d, J = 14.5 Hz, 3H), 3.72 (dd, J = 17.2, 6.3 Hz, 1H).

^{13}C NMR (101 MHz, cdcl_3) δ 176.84, 168.64, 162.43, 147.83, 145.45, 141.97, 137.75, 129.51, 129.40, 126.57, 124.33, 118.51, 115.20, 114.51, 56.59, 55.61, 39.35.

HRMS (TOF-MS APCI+): $[\text{M}+\text{H}]^+$, found 476.1127. $\text{C}_{24}\text{H}_{19}\text{ClN}_5\text{O}_4$ requires 476.1126.

4-(1-(4-chlorophenyl)-5-(3-(4-fluorophenyl)-1,2,4-oxadiazol-5-yl)-4,5-dihydro-1H-pyrazol-3-yl)benzonitrile (3g) (PyOx-7)



Rotary chromatography (Chromatotron) (50% EtOAc/hexane) afforded bright yellow solid. Yield: (0.133 g, 100%), R_f (%17 EtOAc/hexane) 0.30. IR (ATR, cm^{-1}): ν = 3010 (arom.CH), 2917-2861 (C-H), 2228 (C $\equiv$ N str.), 1606 (C=N), 1555 (C=N), 1489 (C=C), 1275 (C-O), 1156, 839 (N-O), 748 cm^{-1} .

^1H NMR (400 MHz, cdcl_3) δ 8.05 (dd, J = 8.4, 5.5 Hz, 2H), 7.84 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.9 Hz, 2H), 7.17 (t, J = 8.0 Hz, 4H), 5.74 (dd, J = 12.6, 6.3 Hz, 1H), 3.92 (dd, J = 17.1, 12.7 Hz, 1H), 3.69 (dd, J = 17.2, 6.3 Hz, 1H).

^{13}C NMR (101 MHz, cdcl_3) δ 177.21, 167.89, 165.82, 145.67, 141.91, 135.65, 132.52, 129.84, 129.75, 129.33, 126.28, 122.21, 118.68, 116.32, 116.11, 114.96, 112.28, 56.31, 39.14.

HRMS (TOF-MS APCI+): $[\text{M}+\text{H}]^+$, found 444.1006. $\text{C}_{24}\text{H}_{16}\text{ClFN}_5\text{O}$ requires 444.1027.

3.3 Optical Characterization of Pyrazoline Derivatives

UV-Visible absorption and fluorescence emission spectroscopy are frequently employed in the literature as effective and practical techniques to examine the photophysical characteristics of materials exhibiting fluorescence properties. Furthermore, time-resolved fluorescence (TRF) spectroscopy is widely used to comprehend the emission kinetics in fluorescent materials as a powerful technique. In this section, the methods for figuring out the photophysical characteristics of pyrazoline derivatives synthesized in the concept of the thesis are going to be outlined with experimental details.

3.3.1 UV-Vis Absorption Measurements

UV-Vis absorption measurements is a spectroscopic technique that allows information about the interaction of light with the material; thus, it has great importance for investigating the photophysical properties of materials. In particular, it enables us to monitor the transitions between the energy levels of a material excited by the incident light. In summary, first, the sample is excited by photons having a fixed wavelength, generated using a full-spectrum light source and

monochromator, during the UV-Vis absorption measurement. Then, the photons that are not absorbed (i.e., photons that are transmitted) by the material in a solution are collected by a photodetector. Here, the target material as dissolved in a solvent is in a cuvette, and it is located between the monochromator and the photodetector. To get an absorption spectrum in the UV-Vis region, the material is continuously excited with photons having different wavelengths adjusted in the desired range by using the monochromator, and the transmitted ones are collected using the photodetector. Lastly, by comparing the intensity of light (i.e., number of photons) passed through the sample cuvette to that of the reference cuvette that is only filled with solvent, the absorption of the target material is ascertained.

In this study, the double-beam UV-Vis absorption spectrophotometer (Hitachi U-2900) was utilized. The quartz cuvettes having an optical path of 1 cm were utilized, which is transparent to UV light. The measurements were carried out at room temperature in the wavelength range of 200–800 nm. To compare the absorption capability of samples synthesized in the concept of this thesis, the concentration of the samples in the solution was kept at 10^{-5} M (i.e., 10 μ M). In addition, the measurements were also performed for solvents with different polarities. Furthermore, the molar extinction coefficient, or so-called molar absorptivity, of the samples was calculated according to the Lambert-Beer law (58).

3.3.2 Steady-State Fluorescence Measurements

Fluorescence spectroscopy is an important technique used for determining and analyzing the photophysical properties of a material. This analytical technique allows us to understand the optical properties of a material in the excited state by visualizing its response under photoexcitation. In summary, first, the target sample is excited by photons having a fixed wavelength, generated using a full-spectrum light source and monochromator (or a laser) during the steady-state fluorescence measurement. The emitted photon by the sample while it comes back from excited-state to ground-state are collected using a photodetector that is positioned perpendicularly to the excitation source. Then, the monochromator positioned in front of the photodetector scans a broad wavelength range to collect the emitted photons having different wavelengths from the sample.

In this study, Hitachi F-4500 Fluorescence Spectrophotometer was utilized to perform the steady-state fluorescence measurements of the synthesized pyrazoline derivatives for their solution phase. All measurements were carried out in a quartz cuvette with four polished windows that enable measurement at right angles to the beam path. In addition to performing the measurements at room temperature, the concentration of solutions was kept at 10^{-5} M (i.e., 10 μ M) to avoid self-absorption effects.

In addition, Andor Solis SR 500i-BL model spectrometer was used to carry out the fluorescence measurements of the samples in solid state (i.e., powder form). To collect the photons emitted from the samples at room temperature, an Intensified Charge Coupled Device (ICCD) detector camera and the appropriate lenses with 1200 lines/mm grid width were utilized. During the measurements, the samples were excited at 350 nm of wavelength by using the Spectra-Physics model triplet Nd-YLFQ-switch pulse laser.

3.3.3 Time-Resolved Fluorescence Measurements

Time-resolved fluorescence spectroscopy is a powerful tool for understanding the photophysical properties and dynamic behavior of a fluorescent material in the excited state. This technique allows us to study the response of a material to light over very short time intervals. In other words, it is an analytical technique that examines how a material fluoresces after exposure to light and how this process changes over time. In summary, after the material is excited with a laser source, the emitted photons while it comes back to the ground state are measured with a very short delay time at a fixed wavelength (e.g., peak wavelength of fluorescence emission). The resulting fluorescence data is analyzed as a graph or spectral changes that show how it changes over time.

In the study, Picoquant Fluotime 200 system was utilized to investigate the emission kinetics of the synthesized pyrazoline derivatives. A pulsed laser diode with a picosecond pulse width was used to excite the sample during the measurements. The measurements were carried out under the 375 nm excitation

wavelength and with a 10 MHz repetition rate, at room temperature. In addition, the time-correlated single photon counting (TCSPC) technique was used to collect the fluorescence emission as a function of time. Finally, to analyze the fluorescence emission decay curves, FluoFit Pro software was used.

3.3.4 Fluorescence Quantum Yield Measurements

The number of emitted photons by a fluorescent material per the number of absorbed photons by it is defined as the fluorescence quantum yield of that material (FL QY), which gives information about the efficiency of the radiative transitions between the energy states (128).

Fluorescence quantum yield measurements are methodologically categorized as relative and absolute measurements. Both techniques are important tools for understanding fluorescence properties and enabling the characterization of materials. Understanding photophysical properties at the molecular level is a fundamental requirement for many applications using fluorescent materials, and these measurement techniques play an important role in this field. Relative fluorescence quantum efficiency is a method to determine the quantum yield of a fluorescent sample compared to a reference sample. In this technique, the quantum yield of the reference sample must first be known. Then the fluorescence intensity of the target sample is compared to that of the reference sample. On the other hand, absolute fluorescence quantum yield measurements are based on the principle of direct measurement without using a reference sample. In this technique, the number of photons absorbed and emitted by the material is directly measured using instruments such as the integrating sphere. In this way, the absolute quantum yield of the target sample is calculated.

In this study, the relative quantum yield measurement technique was used for the samples in solution, whereas the absolute one was utilized for the samples in solid state. In the relative quantum yield technique, the Parker-Rees method was used for the FL QY calculations as follows (128),

$$QY_s = QY_r \frac{F_s A_r n_s}{F_r A_s n_r} \quad (3.1)$$

where QY , F , A , and r are referred to the quantum yield, the spectrally integrated number of photons, the absorbance at the excitation wavelength, and the refractive index of the solvent used in measurements, respectively. Here, the subscript "s" denotes the target sample while "r" is the reference sample. For the relative quantum yield measurements, the quinine sulfate was utilized as the reference dye. The reference dye solution was prepared in 0.5 M H_2SO_4 solution. During the calculation quantum yield of the quinine sulfate solution was taken as 0.55 (129). On the other hand, the absolute quantum yield measurement technique was used for the samples in solid-state. Hamamatsu C11347 Absolute PL Quantum Yield Spectrometer was used for the measurements.

4. RESULTS AND DISCUSSION

In the pursuit of creating unique molecules with adaptable and advantageous properties, many researchers were drawn to the allure of pyrazoline, an important member of heterocycles. Pyrazolines with tunable properties have been widely used in different applications such as optic brighteners of textiles, fibers or papers, fluorescent probes to recognize some ions and metals, organic electronics, and hole-transport materials. After the introduction of a pyrazoline molecule emitting bright blue light with tunable photophysical properties, numerous pyrazoline derivatives have been prepared for diverse applications (see Figure 4.1) (130–133).

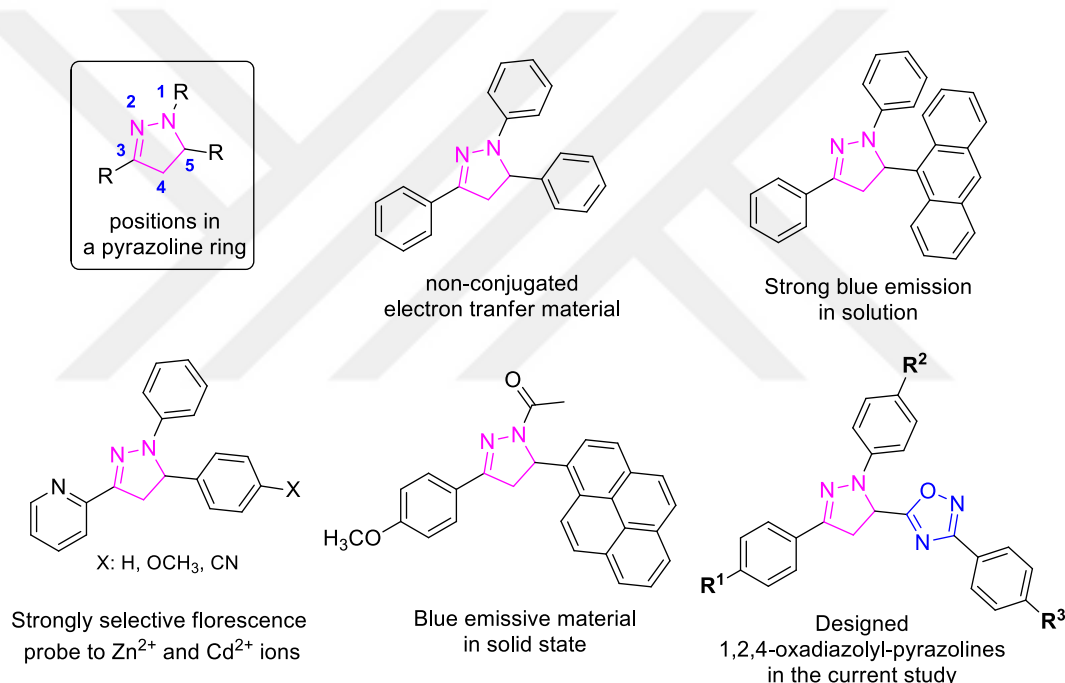


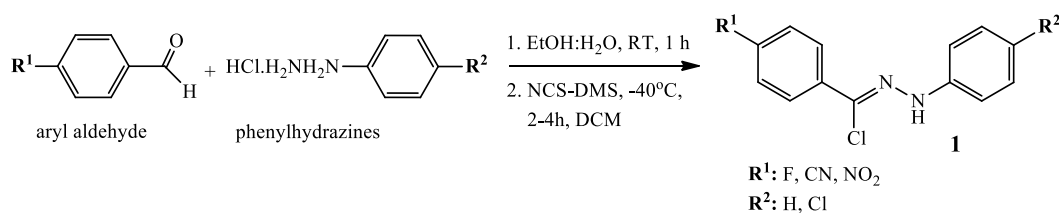
Figure 4.1. Some fluorescent pyrazoline-based structures and designed 1,2,4-oxadiazole substituted pyrazoline molecules.

The electron-donating ability of a pyrazoline ring originates from the N atom having lone pairs located in position-1 (N-1) in the ring. Furthermore, introduction of different substituents to this position induces significant changes in the photophysical properties of pyrazoline compounds. Improvement of optical properties in pyrazoline compounds can also be done by changing the substitution pattern at the C-3 and C-5 phenyl rings. Due to the potential for charge transfer (CT)

emission, there is a continuous interest in the photophysics of N-phenyl-substituted five-membered rings and their derivatives, both in aqueous/waterless solvents. Some studies on non-conjugated 5-position of pyrazoline-based photosensitizers affecting the photophysical properties and performance of dye-sensitized solar cells (DSSCs) revealed an increase in absorption maxima, electrochemical properties and DSSC performance which was induced by increasing electron-donating power. Similarly, some 1,3,5-triaryl-substituted pyrazolines have shown some intramolecular nonconjugated electron transfer and fluorescence properties (134). In this context, we decorated the pyrazoline nucleus with different substituents on the aryl and 1,2,4-oxadiazole rings since it would increase the conjugation length, due to the presence of an additional double bond in alternate arrangements with the phenyl rings. Besides, we elucidated the substituent effects of aryl groups on the absorption and fluorescence properties of this new aryl-heteroaryl substituted pyrazoline scaffold (see Figure 4.1). To the best of our knowledge, these newly designed pyrazoline-1,2,4-oxadiazole derivatives are novel compounds and unstudied in term of photoluminescence and optical properties. However, only one study is available in the literature, some similar derivatives having a pyrazoline-1,2,4-oxadiazole hybrid skeleton have been prepared by a multistep synthetic method and some biological activity studies were conducted for them (135).

4.1 Preparation of Starting Materials

In the current study, firstly, we prompted for the synthesis of two sets of precursor compounds using simple and convenient methods. First precursors, *C,N*-diaryl substituted hydrazonyl chlorides **1**, were simply prepared in two steps by following early reported procedures. The structures of *C,N*-diaryl substituted hydrazonyl chlorides **1** (Scheme 4.1) were elucidated through IR and by comparing with relevant data (IR, NMR) reported in the literature (136,137). The synthesis and reaction yields of *C,N*-diarylhydrazonyl chlorides **1** is also given in Table 4.1.

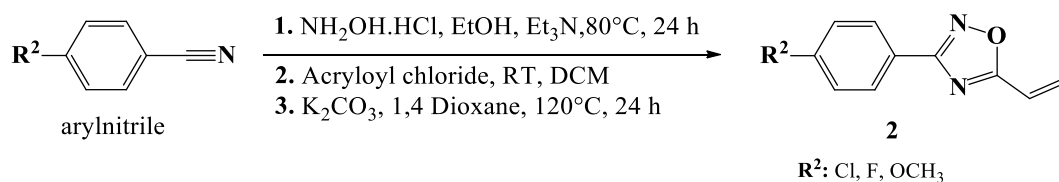


Scheme 4.1. Synthesis of C,N-diarylhydrazonyl chlorides **1**.

Table 4.1. Synthesis and reaction yields of C,N-diarylhydrazonyl chlorides **1**.

Compound	R ¹	R ²	Yield (%)	m.p. (°C)
1a	F	H	88	117-119
1b	NO ₂	H	91	151-153
1c	CN	H	60	145-146
1d	NO ₂	Cl	96	219-220
1e	CN	Cl	94	215-217

The second precursor compounds, aryl substituted vinyl-1,2,4-oxadiazoles **2**, were prepared over three-step synthetic protocol (Scheme 4.2) as reported in the literature. The first step involved the reaction of 4-substituted benzonitriles with hydroxylamine in the presence of Et₃N to give 4-substituted benzamidoximes. In the second step, 4-substituted benzamidoximes were reacted with acryloyl chloride in DCM to give N-acrylobenzamidoximes which were subsequently converted into aryl vinyl 1,2,4-oxadiazoles **2** using K₂CO₃ with moderate-good yields (58-75%) in the last step (Table 4.2). Then, the structures of arylvinyl-1,2,4-oxadiazoles **2** were elucidated by relevant IR, NMR data as reported in the literature (138–140).



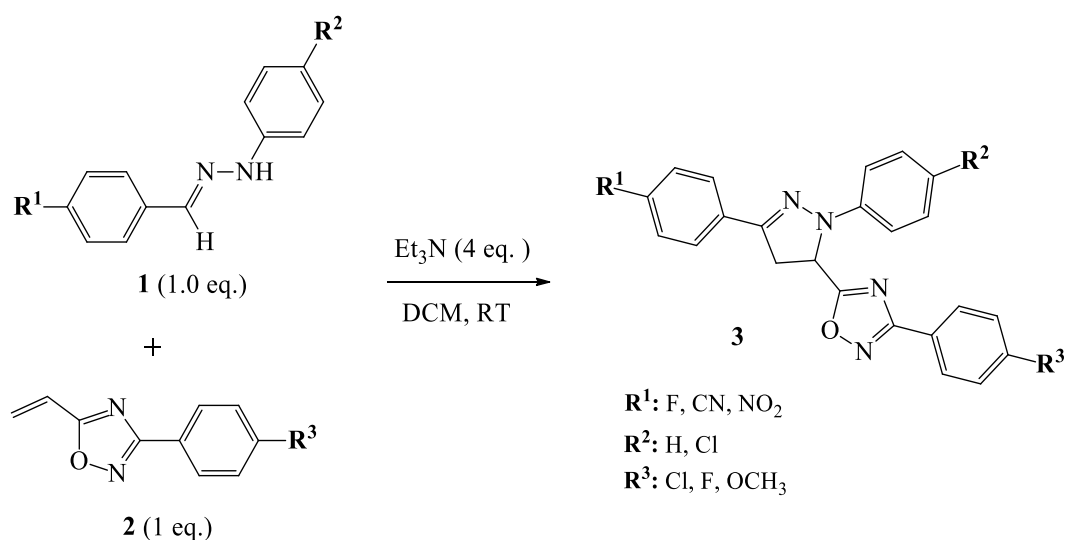
Scheme 4.2. Synthesis of aryl vinyl-1,2,4-oxadiazoles **2**.

Table 4.2. Reaction conditions and yields of aryl vinyl 1,2,4-oxadiazoles **2**.

Product	R ²	Temp.(°C)	Time (h)	Yield (%)	m.p.
2a	OCH ₃	120	24	58	59-61
2b	Cl	120	24	75	63-65
2c	F	120	24	66	50-52

4.2 Synthesis and Characterization of 1,3-diaryl substituted-5-(1,2,4-oxadiazolyl)pyrazolines (**3**)

In the second part, we continued the synthesis of 1,2,4-oxadiazole-bearing pyrazolines (**3**) via 1,3-dipolar cycloadditions of nitrile imines under very mild conditions (Scheme 4.3). To this end, all hydrazone chlorides (**1a-1c**) were reacted with aryl vinyl-1,2,4-oxadiazoles (**2a-2e**) in the presence of triethylamine in DCM at room temperature. All the 1,2,4-oxadiazolyl diarylpyrazolines (**3a-3g**) were isolated in good to excellent yields after purifying by FCC or RC (radial chromatography). Cycloaddition product **3g** was obtained with quantitative yields from the reaction of hydrazone chloride **1e** (R¹:CN, R²:Cl) and vinyl-1,2,4-oxadiazole **2c** (R³:F). On the other hand, the lowest yield (79%) was attained for the product **3c** (R¹:NO₂, R²:Cl, R³:F (Table 4.3, entry 3). Current cycloaddition reaction between nitrilimines (**1**) and aryl vinyl-1,2,4-oxadiazoles (**2**) were found very regioselective because only one regioisomer, 5-pyrazoline, was isolated and characterized in NMR analyses of the cycloaddition products (**3**).



Scheme 4.3. Synthesis of novel 1,3-diaryl substituted-5-(1,2,4-oxadiazolyl)pyrazolines **3**.

Table 4.3. Reaction yields and conditions for the synthesis of novel 1,3-aryldisubstituted-5-(1,2,4-oxadiazolyl)pyrazolines **3**.

3a-g

Entry	Product	Code	R ¹	R ²	R ³	Temp. (°C)	Time (h)	Yield (%)
1	3a	PyOx-1	F	H	Cl	20	48	88
2	3b	PyOx-2	F	H	F	20	24	83
3	3c	PyOx-3	F	H	OCH ₃	20	48	80
4	3d	PyOx-4	NO ₂	Cl	Cl	20	48	96
5	3e	PyOx-5	NO ₂	Cl	F	20	72	79
6	3f	PyOx-6	NO ₂	Cl	OCH ₃	20	96	91
7	3g	PyOx-7	CN	Cl	F	20	48	100

The structures of cyclization products **3a-3g** were characterized using IR, ¹H-NMR, ¹³C-NMR, and MS spectral data. If we briefly explain the structural characterization of the products through one example. The main IR bond stretching of product **3a** at 2921-2853 cm⁻¹ (aliph.CH), 1594-1553 cm⁻¹ (C=N), 1267 cm⁻¹ (C-O), and 828 cm⁻¹ (N-O) simply showed the formation of expected product (Figure 4.2).

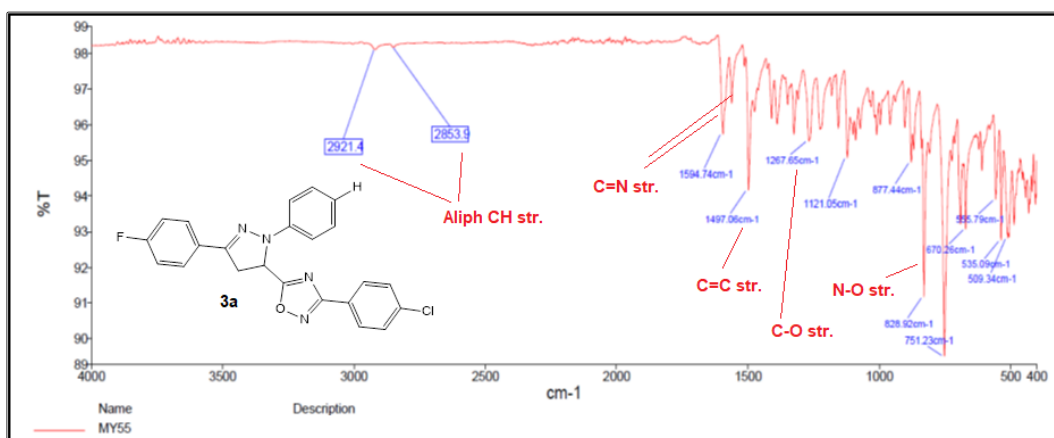


Figure 4.2. Infrared (IR) spectrum of product **3a** (i.e., PyOx-1).

Besides, when we analyze the proton NMR chemical shifts of product **3a** in Figure 4.3, it showed the signals of three protons (Hh, Hi, Hj) in pyrazoline ring at 3.6, 3.8, and 5.6 ppm as a doublet of doublets (dd) which supported the structure of the pyrazoline product **3a** (Table 4.4).

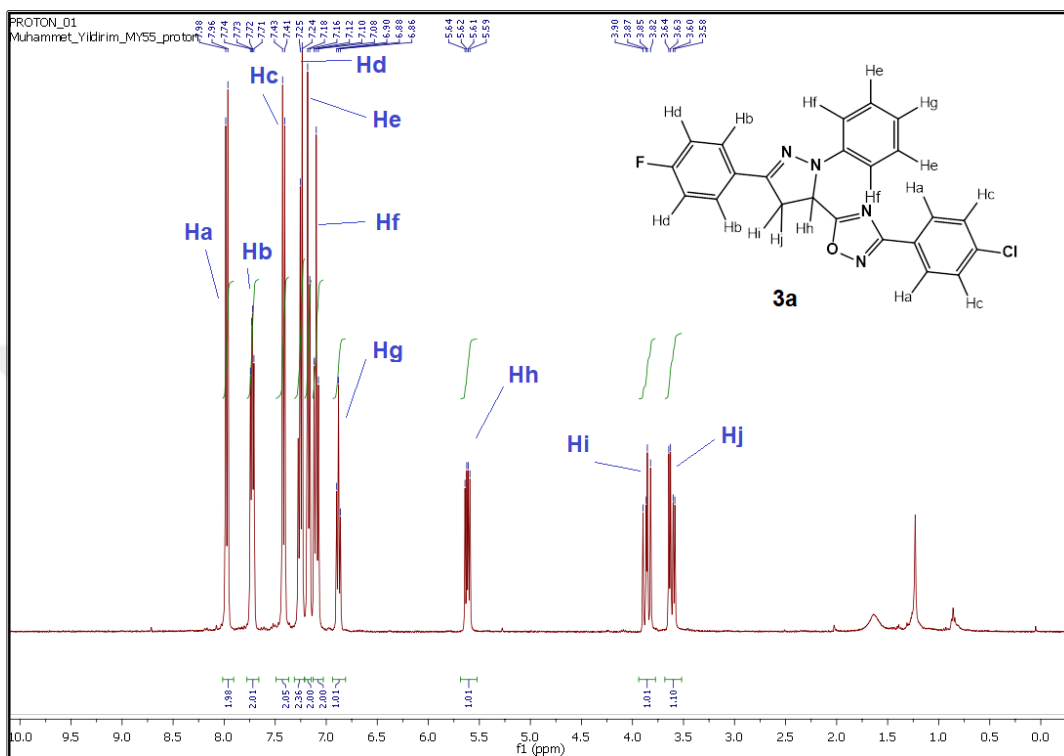


Figure 4.3. Proton nuclear magnetic resonance (^1H NMR) spectrum of **3a** (i.e., PyOx-1).

^{13}C NMR spectra of product **3a** showed specific pyrazoline and 1,2,4-oxadizole C signals (C-1, C-3, C-4, C-16, C-17) at around 178, 167, 164, 56 and 39 ppm in Figure 4.4, respectively (Table 4.5).

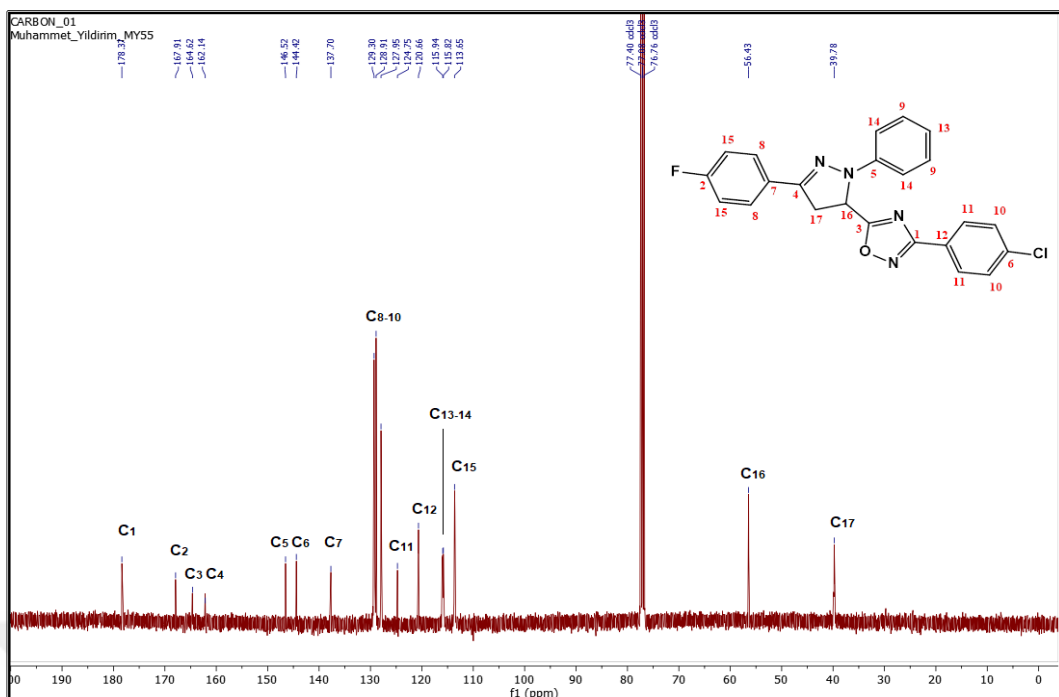
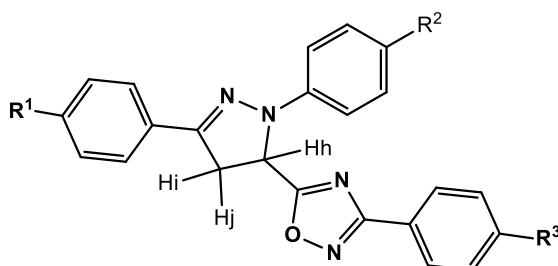
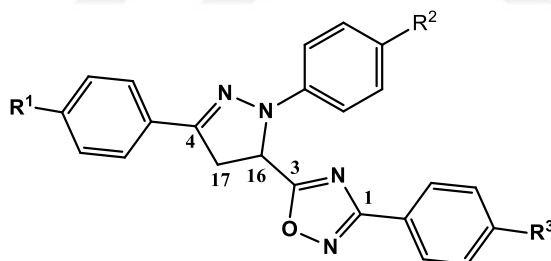


Figure 4.4. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectrum of the product **3a** (i.e., PyOx-1).

All the 1,2,4-oxadiazolyl-pyrazoline derivatives **3a-3g** were characterized using the indicative IR, ^1H -NMR, and ^{13}C -NMR data as shown in the example spectra above. In general, IR spectra of products **3a-3g** showed characteristic peaks for aromatic CH, aliphatic CH, C=N, C-O, NO_2 and $\text{C}\equiv\text{N}$ bond stretching vibrations at around 3006-3021, 2981-2846, 1606-1553, 1275-1250, 1513-1324 and 2228 cm^{-1} , respectively (Table 4.4). The ^1H NMR spectra of compounds **3a-3g** showed proton signals in pyrazoline ring at around 5.62-5.78, 3.86-3.97, and 3.61-3.88 ppm (Table 4.4). Also, ^{13}C -NMR spectra of **3a-3g** derivatives showed the C1, C3, C4, C16, C17 signals in isoxazoline-1,2,4 oxadiazole ring system at around 176-178, 167-168, 164-165, 56.3-56.7, and 39.1-39.9 ppm, respectively. Other carbon signals such as O- CH_3 (55-56 ppm) for **3d-3e** also supported the structure of the expected products (Table 4.5).

Table 4.4. Indicative IR and ¹H NMR data for the compounds **3a-3g**.

Product		IR (vmax/cm ⁻¹)			¹ H-NMR (δ,ppm)		
3	arom.CH	C=N	C-O	N-O	Hh	Hi	Hj
a	3020	1594	1267	828	5.62	3.86	3.61
b	3006	1595	1261	830	5.64	3.88	3.64
c	3021	1594	1257	834	5.63	3.95	3.64
d	3011	1595	1250	846	5.77	3.95	3.72
e	3013	1590	1275	812	5.78	3.97	3.74
f	3006	1593	1259	846	5.75	3.94	3.88
g	3010	1606	1275	839	5.74	3.92	3.69

Table 4.5. Detailed ¹³C NMR data of compounds **3a-3g**.

Product		¹³ C-NMR (δ, ppm)				
3		C1	C3	C4	C16	C17
a		178.3	167.9	164.6	56.4	39.7
b		178.4	167.7	164.5	56.6	39.9
c		177.8	168.3	164.5	56.5	39.7
d		177.1	167.9	147.7	56.3	39.1
e		177.5	168.4	166.4	56.7	39.5
f		176.8	168.4	162.4	56.5	39.3
g		177.2	167.8	165.8	56.3	39.1

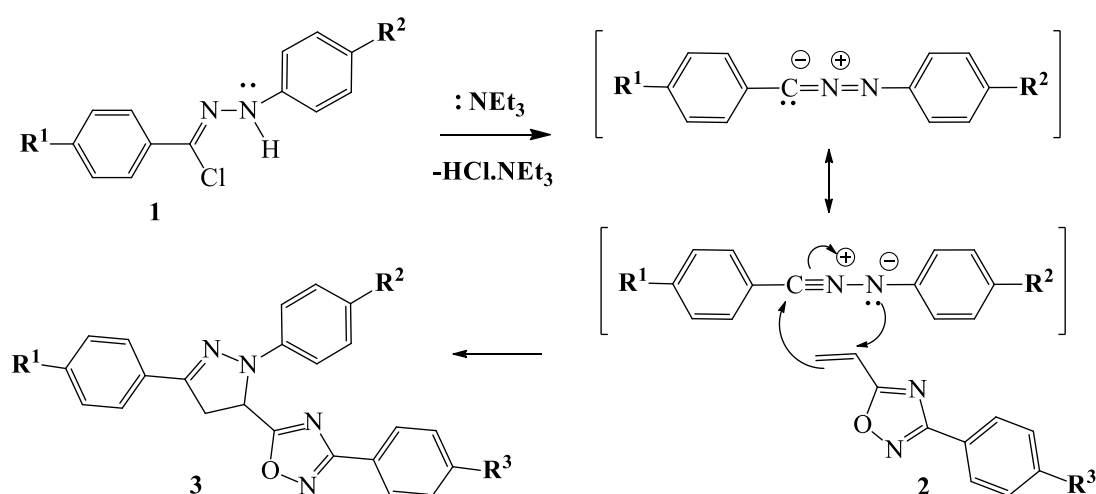
Accurate mass results were also provided for the products **3a-g** and they are all found in accordance with the expected high-resolution mass data (Table 4.6).

Table 4.6. Time-of-flight mass spectrometry (TOF-MS) results for the products **3a-3g**.

HR-MS results			
Product	m/z (calc.d)	m/z (found)	ionization method
3a	[M+H] ⁺ , 419.1075	419.1070	APCI ⁺
3b	[M+H] ⁺ , 403.1370	403.1348	APCI ⁺
3c	[M+H] ⁺ , 415.1570	415.1562	APCI ⁺
3d	[M] ⁺ , 479.0551	479.0526	ESI ⁻
3e	[M+H] ⁺ , 464.0905	464.0905	APCI ⁺
3f	[M+H] ⁺ , 476.1126	476.1127	APCI ⁺
3g	[M+H] ⁺ , 444.1027	444.1006	APCI ⁺

All spectral and physical data of products were presented in the experimental section, also the supportive spectra (IR, NMR, MS) for all products **3a-3g** were added in the appendices section.

A suitable mechanism affording the products **3** via 1,3-dipolar cycloadditions of nitrile imines with vinyl-1,2,4 oxadiazole **2** is proposed below. (Scheme 4.4).



Scheme 4.4 Mechanism for the formation of novel 1,3-diarylsubstituted-5-(1,2,4-oxadiazolyl)pyrazolines **3a-3g**.

4.3 Photophysical Properties of Pyrazoline Derivatives

This section presents the photophysical properties of the pyrazoline derivatives comprising 1,2,4-oxadiazole ring and different electron-donating and electron-withdrawing groups. Hereafter, the compounds enumerated as **3a-3g** in the experimental section will be denoted as **PyOx-1-PyOx-7** in this section, respectively.

4.3.1 Pyrazoline Derivatives in Solution

To investigate the photophysical properties of the synthesized pyrazoline-based compounds in solution, the UV-Vis absorption and steady-state fluorescence spectroscopy techniques were used. In the first step, the UV-Vis absorption measurements were carried out at room temperature. The toluene (C_7H_8) was chosen as a host medium (i.e., solvent) to dissolve the samples, and the solutions were prepared at a concentration of 10^{-5} M for the measurements.

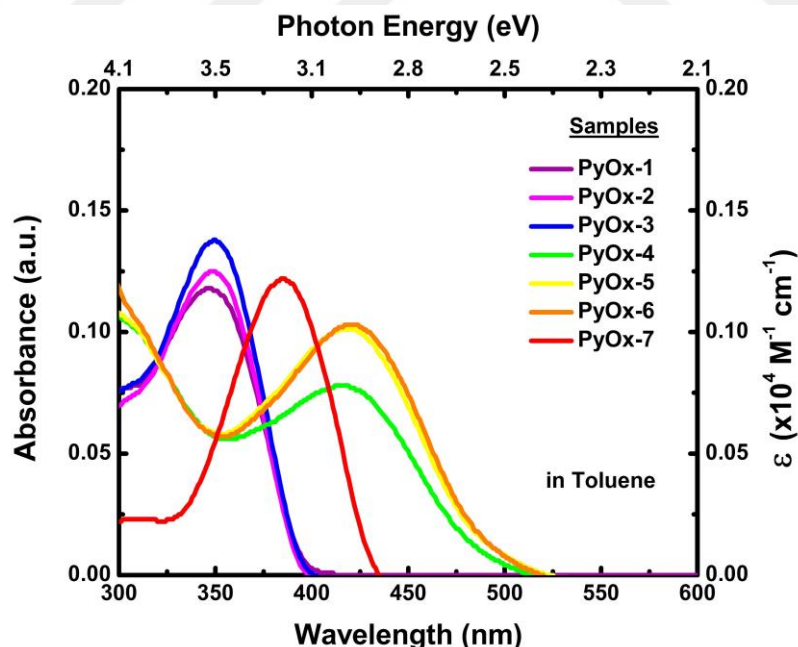


Figure 4.5. UV–Vis absorption spectra of the pyrazoline derivatives in toluene. The right vertical axis represents the absorbance, while the left depicts the corresponding molar extinction coefficients (ϵ).

Figure 4.5 shows the evolution of absorption features of the pyrazoline derivatives with their molar extinction coefficient (ϵ) as a function of excitation wavelength. To analyze the absorption properties of the synthesized compounds, we have classified them into three main groups (See Figure 4.6). The compounds in the first group (PyOx-1–PyOx-3) comprise a non-substituted aryl ring in position 1 and a fluorine (F)-substituted aryl ring in position 3. However, at position 5, they have different substituents on the heteroaryl ring such as chlorine (-Cl) and fluorine (-F) or methoxy (-OCH₃), respectively. As can be seen in Figure 4.5, an absorption peak has appeared at around 348 nm. Although the position of the absorption maxima exhibits a few nm of shift (~ 2 nm) in the spectrum, no significant changes were observed in the shape of the absorption curve with changing the substituent (i.e., -Cl, -F, and -OCH₃) on the heteroaryl moiety (i.e., 1,2,4-oxadiazole) located at position 5 of the pyrazoline ring. In addition, it has been observed that the molar absorptivity of the compound increases as the substituent attached on the electron-withdrawing oxadiazole ring is changed to one that has a relatively strong electron-releasing ability.

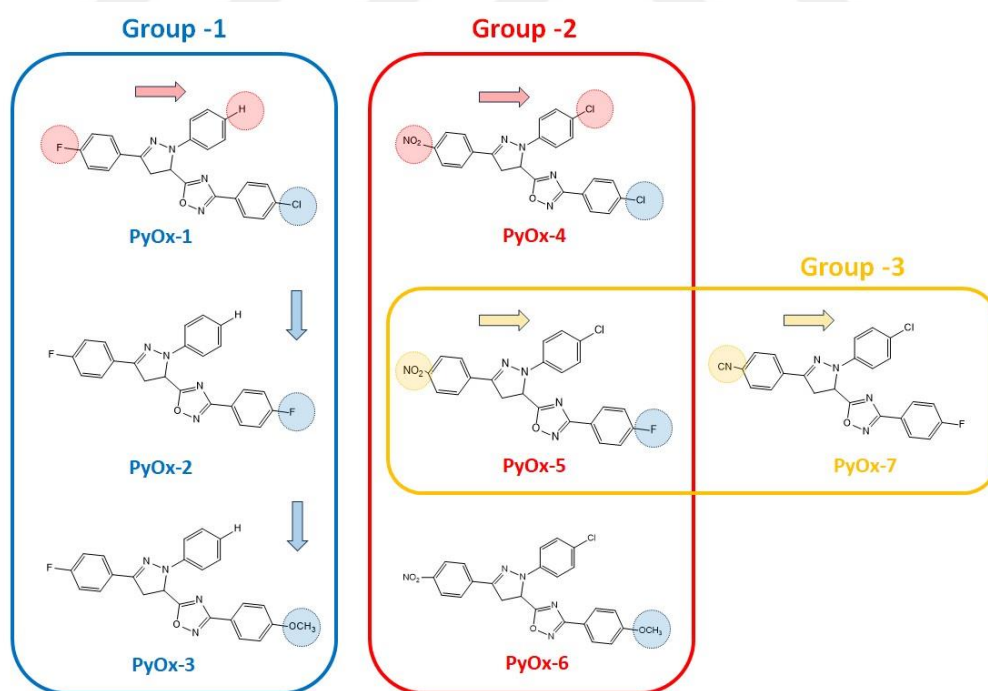


Figure 4.6. Classification of the samples according to the changes in the substituents at positions 1, 3, and 5 of the pyrazoline ring. The colored circles and arrows indicate the substituents that have been changed, as well as their position and direction of change in the group of samples, respectively.

For instance, when the -Cl was replaced with the -OCH₃ group on the 1,2,4-oxadiazole moiety (i.e., PyOx-1 and PyOx-3), the compound's molar absorptivity increased by 17%. On the other hand, the groups on the aryl moieties located at positions 1 and 3 of the pyrazole ring were changed in the second group of the sample to analyze the substituent effect. Here, the compounds (PyOx-4-PyOx-6) have a chlorine (-Cl) substituted aryl ring in position 1 and a nitro (-NO₂) substituted aryl ring in position 3, while the substituent on the oxadiazole moiety was changed with chlorine (-Cl) and fluorine (-F) or methoxy (-OCH₃), respectively, like in samples in the first group. The absorption properties of this group exhibit significant changes as compared to those of the compounds in the first group. For instance, it is seen that the absorption capability of the sample is enhanced with a 100 nm shift in the starting point of the absorption to the longer-wavelength side of the electromagnetic spectrum. In addition, the absorption maxima of the samples are redshifted by about 70 nm, while a new absorption shoulder appears on the high-energy side of the spectrum. As in the first group, the molar absorptivity of the compounds in the second group enhanced based on the relative electron-donating ability of the substituent on the oxadiazole ring at position 5 of the pyrazoline ring. It was found that an increment of 32% in the molar absorptivity of the PyOx-6 as compared to that of the PyOx-4. Although the compounds in the second group have a 2-fold increase in their molar absorptivity compared to the first group when changing the substituent on the oxadiazole moiety, the molar absorptivity is still generally higher in the first group compounds.

To better understand the effect of the electron-withdrawing ability of the substituent located on the aryl moiety at position 3 on the absorption features of the compounds, the nitro group (-NO₂) was replaced to the cyano group (-CN) which has a relatively lower electron-withdrawing ability compared to the nitro group (see Group 3 in Figure 4.6). The comparison of the absorption profiles of the PyOx-5 and PyOx-7, which include the nitro (-NO₂) and the cyano (-CN) groups, respectively, clearly demonstrates that the ground-state photophysical properties of the compound, such as the spectral position of the absorption maximum and the molar absorptivity, are strongly influenced by the electron-withdrawing ability of the substituent. As can be seen in Figure 4.5, the spectral position of the absorption maximum for the PyOx-7 comprising the -CN group emerges at 385 nm, whereas

it shifts towards the longer-wavelength side of the spectrum (i.e., to 419 nm) for the PyOx-5 having the $-\text{NO}_2$ group. In addition, it was observed that the presence of the $-\text{CN}$ group in position 3 gives rise to an increase in the maximum molar absorptivity by about 21% compared to that of the PyOx-5, which comprises the $-\text{NO}_2$ group.

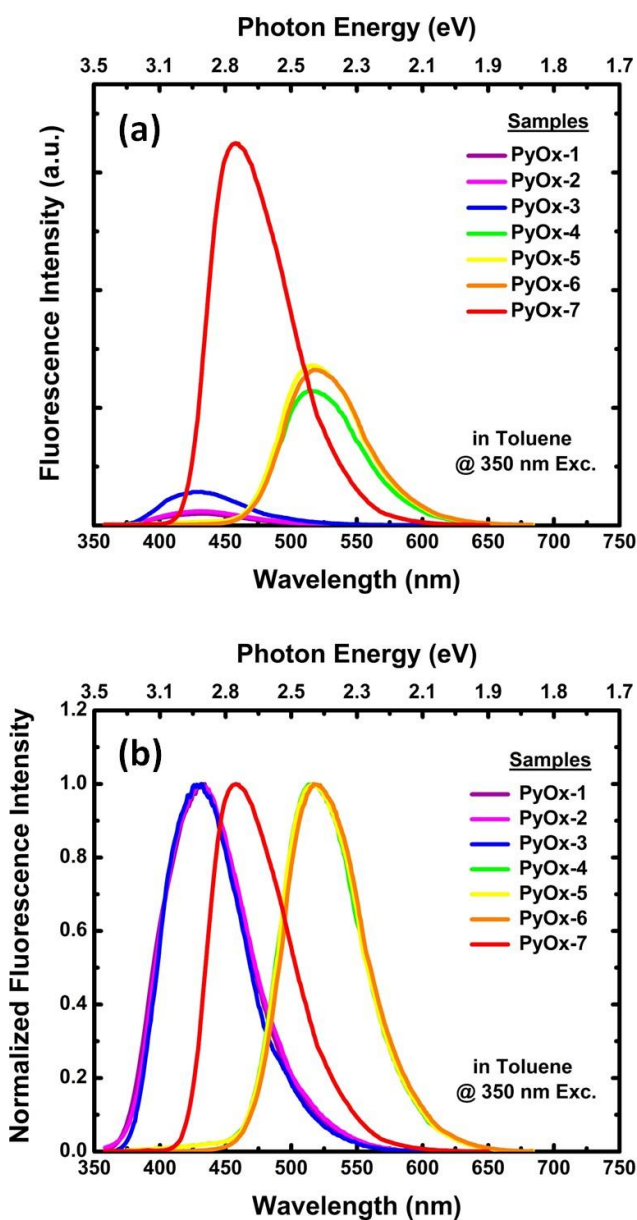


Figure 4.7. (a) Fluorescence spectra of the pyrazoline derivatives in toluene at room temperature under 350 nm excitation. (b) Normalized version of the fluorescence spectra given in (a) for the pyrazoline derivatives in toluene.

In addition to studying the UV-Vis absorption properties of pyrazoline derivatives in toluene, we investigated their photophysical properties for the excited state using steady-state fluorescence spectroscopy technique. To avoid the self-absorption effect, which can result in a large variation in the energy and shape of the emission spectrum, the measurements were conducted in the dilute solution of the samples (i.e., 10^{-5} M in toluene). The measurements were also carried out at room temperature, with an excitation wavelength of 350 nm.

Figure 4.7 shows the fluorescence emission profiles of the pyrazoline derivatives (i.e., PyOx-1 – PyOx-7) in toluene. It is clearly seen from Figure 4.7a that the first group samples (i.e., PyOx-1–PyOx-3) exhibit poor fluorescence properties, whereas the relatively high emission in the second group (i.e., PyOx-4 – PyOx-6). This reveals that the positions 1 and 3 on the pyrazoline rings govern the emission kinetics of the synthesized 1,3-diarylsubstituted-5-(1,2,4-oxadiazolyl)pyrazoline derivatives. In addition, it was observed that the fluorescence intensity increases when the strong electron-withdrawing group -NO₂ (i.e., PyOx-5) is changed with the relatively weak electron-withdrawing group -CN (i.e., PyOx-7). This result indicates that the photophysical properties of the samples are strongly affected by the electron-withdrawing ability of the substituent attached to the aryl moiety at position 3 of the pyrazoline ring. On the other hand, the spectral position of the fluorescence emission has been significantly affected by the electron-withdrawing ability of the substituent at position 3. As compared to the emission profile of the PyOx-5 with that of the PyOx-7, there are 58 nm of blueshift in the spectral position (see Figure 4.7b). However, no substituent effect on the spectral position of the fluorescence emission was observed when analyzing the emission profiles of the samples in the first and second groups individually. The fluorescence emission of the samples (i.e., PyOx-1–PyOx-3) in the first group appears at about 431 nm, whereas the samples i.e., PyOx-4–PyOx-6) in the second group exhibit fluorescence emission around 518 nm. Here, it is obviously seen from Figure 4.7b that the substituents, -Cl, -F, and -OCH₃, do not affect the emission profile spectrally. Even though there is no change in the spectral position, the substituent of the -OCH₃, which is a strong electron-donating group, slightly enhances the emission intensity in PyOx-3 (see Figure 4.7a, blue solid line). The significant shift in the spectral position in the fluorescence emission of the

compounds in the Group-2 and Group-3 can be attributed to the strong electron-withdrawing nature of the -CN and the -NO₂ groups, leads to decrease in the energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of a molecule.

Furthermore, to better analyze the effect of the substituents on the excited state photophysical properties of the compounds based on the pyrazoline-1,2,4-oxadiazole hybrid skeleton, we also calculated the fluorescence quantum yield (FL-QY) of the samples using a reference dye with a known FL-QY. To this end, we utilized the quinine sulfate solution in 0.5 M H₂SO₄ solution as a reference dye, which has 54.6% FL-QY (141–143).

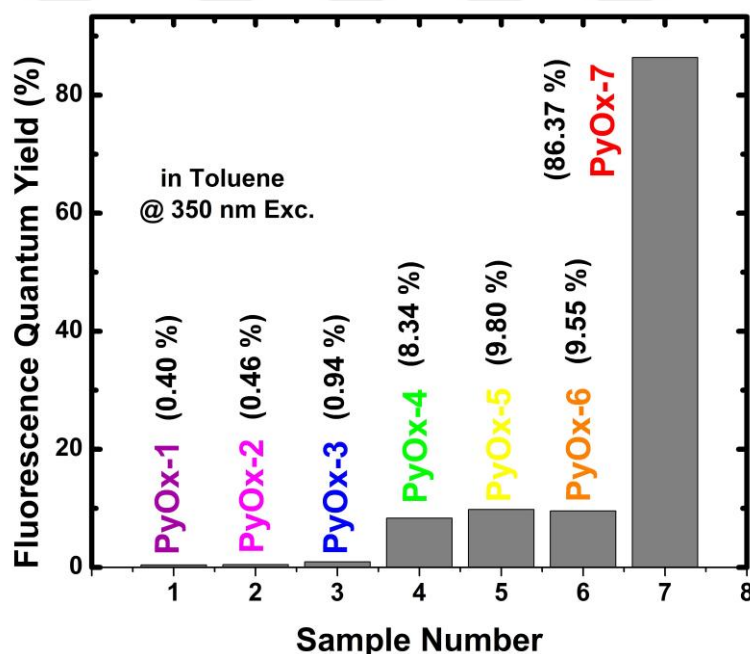


Figure 4.8. Relative fluorescence quantum yields (FL-QYs) of the pyrazoline derivatives in toluene at room temperature under 350 nm excitation. The FL-QY values were determined using the quinine sulfate as the reference dye in 0.5 M H₂SO₄ solution.

The bar graph in Figure 4.8 depicts the relative fluorescence quantum yields (FL-QYs) of the pyrazoline derivatives in toluene. It was found that all samples in the first group have very low FL-QYs, less than 1%. On the other hand, the changing of the substituents -H at position 1 and -F at position 3 with the -Cl and -NO₂ groups, respectively, gave rise to an increase in FL-QY in the second group of

samples. The FL-QYs of the compounds in the Group-2 reached up to 9.80% with about 10-fold enhancement. In addition, a highly remarkable enhancement was observed in the FL-QY by introducing the -CN group instead of the -NO₂ group at position 3. Compared to PyOx-5, the FL-QY of PyOx-7 exhibits a nearly 9-fold increase, reaching 86.4%. The increment in the FL-QY can be explained by minimizing non-radiative decay processes, such as internal conversion and intersystem crossing due to the electron-withdrawal ability of the substituents. With fewer non-radiative pathways, the molecule is more likely to undergo fluorescence (i.e., radiative processes), leading to higher fluorescence quantum yield.

4.3.2 Effect of Solvent Polarity

Understanding the impact of solvent polarity on the emission profile of fluorescent molecules is crucial to studying their photophysical properties. The emission characteristics of a fluorescent solute are significantly influenced by the solvent environment surrounding it. For instance, in a polar solvent, the solute generally experiences a higher degree of solvation, affecting its molecular geometry and electronic structure. This makes the energy levels of the excited state more sensitive to solvent polarity. The stabilization of the excited state is reduced in polar environments, which results in a decrease in the energy gap between the ground and excited states. This phenomenon is known as the solvent effect, also called solvatochromism, and leads to a redshift in the fluorescence emission spectrum. On the other hand, in nonpolar solvent systems, the solute experiences less solvation, leading to a more stabilized excited state, which results in a blueshift in the emission spectrum. Consequently, the polarity of the solvent is a crucial factor in modulating the fluorescent properties of molecules. Therefore, we repeated the absorption and fluorescence measurements for all pyrazoline derivatives in a solvent with a polarity different from that of toluene used in the previous part.

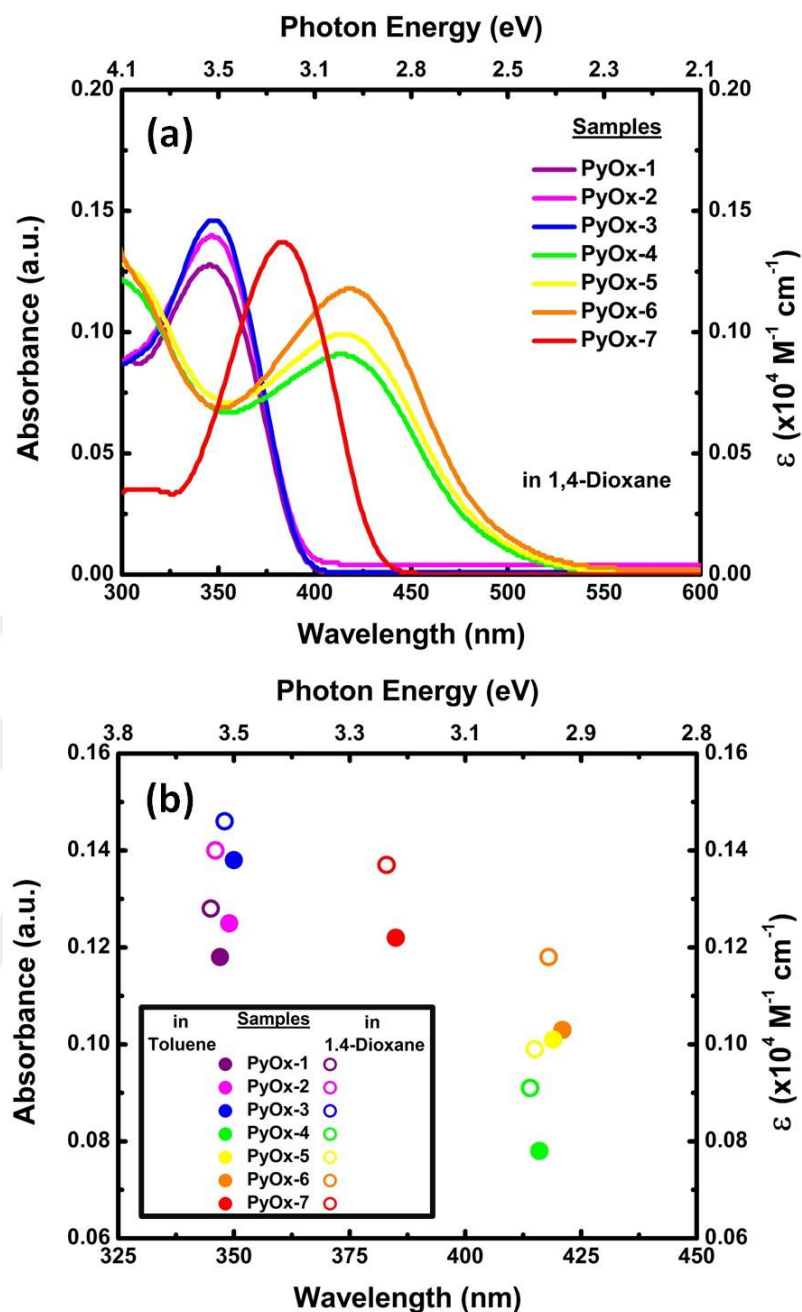


Figure 4.9. (a) UV–Vis absorption spectra of the pyrazoline derivatives in 1,4-dioxane. (a) Comparative representation of the absorption features for the pyrazoline derivatives in different solvent mediums (i.e., toluene and 1,4-dioxane). The right vertical axis represents the absorbance, while the left depicts the corresponding molar extinction coefficients (ϵ).

Figure 4.9a shows the UV-Vis absorption curves of the pyrazoline derivatives in 1,4-dioxane. Here, to observe the effect of solvent polarity on their photophysical properties, 1,4-dioxane, which is a polar aprotic solvent due to the presence of oxygen atoms in its structure and has a higher polarity compared to toluene, was used during the measurements. It was observed that the increasing solvent polarity

does not dramatically affect the general behavior in the evolution of the absorption features of the pyrazoline derivatives. For instance, the molar absorptivity of the compounds is enhanced depending on the substituents attached to the oxadiazole ring at position 5, but the spectral position of the absorption maximum remains considerably unaffected. In contrast, introducing an electron-withdrawing group at position 3 gives rise to dramatic changes both in the spectral position of the absorption and the molar absorptivity. For instance, it is seen that the absorbance band experiences a significant redshift and a reduction in absorptivity as the electronegativity of the substituent increases.

As compared the absorption profiles in the frame of full spectrum, the shape of the absorption curve for each compound remains almost unchanged with the increasing solvent polarity (see Figures 4.5 and 4.9a). To better analyze the solvent polarity effect on the absorption features, the wavelengths corresponding to the absorption maxima, and the molar absorptivity values of the compounds were also given in a graph for both toluene and 1,4-dioxane (see Figure 4.9b). It is clearly seen that all compounds exhibit a slight blue shifted behavior in their absorption spectra with increasing solvent polarity. In addition, the molar absorptivity of compounds is in the increasing trend with increasing polarity of the solvent surrounding the molecules. It is clearly seen that all compounds exhibit slightly blue-shifted behavior (max. 4 nm) in their absorption spectra with increasing solvent polarity. In addition, the molar absorptivity of compounds is in the slightly increasing trend (max. 12%) with increasing polarity of the solvent surrounding the molecules. All the findings indicate that increasing solvent polarity does not significantly affect the ground state of the compounds in terms of structural and electronic properties.

On the other hand, the solvent effect was also studied in the emission properties of the synthesized pyrazoline derivatives. Figure 4.10 depicts the fluorescence emission curves for the pyrazoline derivatives in 1,4-dioxane. It was found that the emission maxima are located around 432 nm for the samples in Group-1 (i.e., PyOx-1 – PyOx-3), whereas it appears at about 542 nm for the samples in Group-2 (i.e., PyOx-4 – PyOx-6). Besides, the emission peak emerges at 466 nm for PyOx-7.

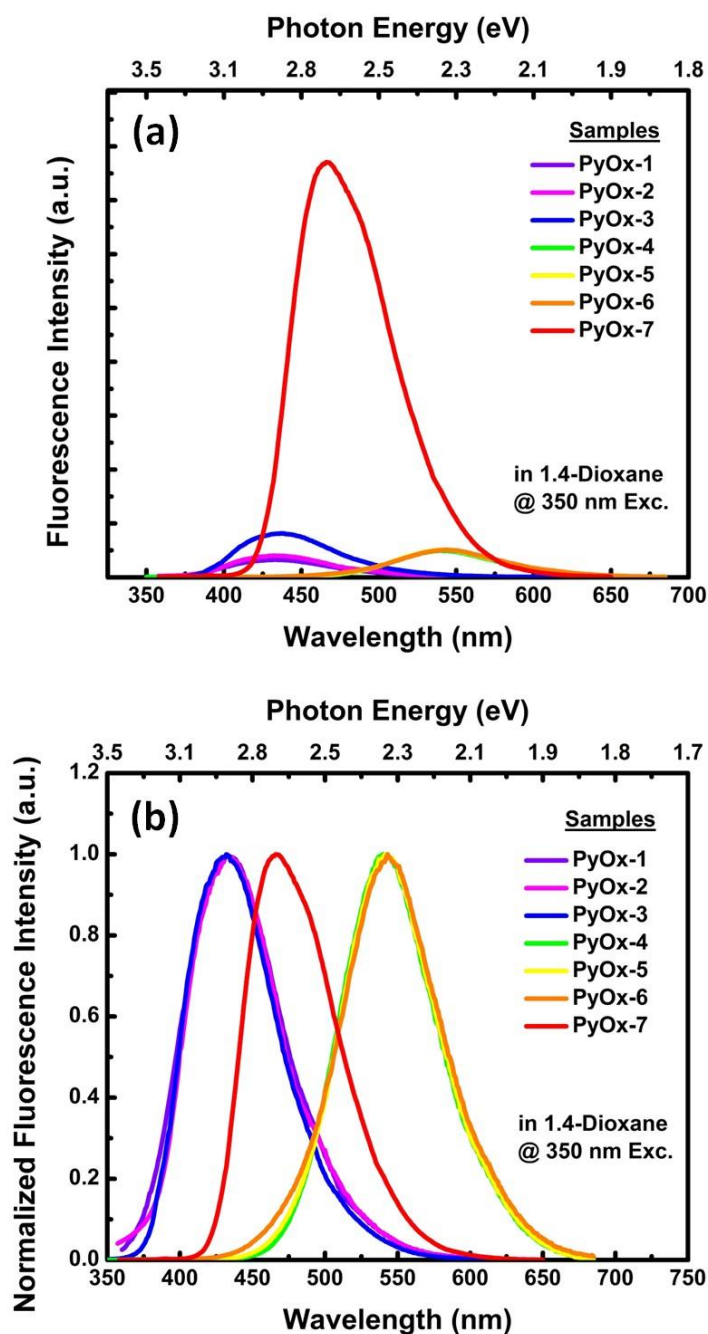


Figure 4.10. (a) Fluorescence spectra of the pyrazoline derivatives in 1,4-dioxane at room temperature under 350 nm excitation. (b) Normalized version of the fluorescence spectra given in (a) for the pyrazoline derivatives in 1,4-dioxane.

Like in the case of the fluorescence measurements in toluene, here, the group of substituents located on the 1,2,4-oxadiazole ring does not exhibit a remarkable effect on the emission properties of the compounds spectrally. However, the electron-withdrawing ability of the substituent at position 3 has a crucial role in tuning the photophysical properties of the pyrazoline derivatives. By increasing the electron-withdrawing ability of the substituent (i.e., from -CN to -NO₂), the

emission is shifted about 78 nm to the longer-wavelength side of the spectrum, which is 20 nm higher than the shift in toluene. The compounds in the first group, PyOx-1 to PyOx-3, exhibit behavior in their emission profiles that is independent of solvent polarity (i.e., max. 2 nm redshift). This can be attributed to the weak electron-withdrawing nature of the -F at position 3. On the other hand, as the solvent polarity increases, we observed a strong polarity-dependent redshift (i.e., 26 nm) in the fluorescence emission of the second group of samples, PyOx-4 to PyOx-6, according to the shift in toluene. This redshift is about 6 nm for PyOx-7 compared to the emission maxima between toluene and 1,4-dioxane. The highly polarity-dependent fluorescence emission properties (i.e., bathochromic shift) in these compounds can be explained by the intermolecular interactions (i.e., dipole-dipole interactions) between the solute and the solvent molecules (58). Briefly, substituents having an electron-withdrawing nature, such as halogens (F, Cl, Br, and I), nitro groups (NO₂), and cyano groups (CN), pull electron density away from the rest of the molecule. During this process, a region of partial positive charge (δ^+) is created, while a region of partial negative charge (δ^-) is formed through the molecule. This leads to a charge separation in the structure of the molecule, which results in the creation of an electric dipole. The magnitude of the net dipole moment of the molecule is proportional to the amount of charge separation and the distance between the charges, which depends on the electron-withdrawing ability of the substituent. As a result, molecules with high dipole moments tend to have strong intermolecular interactions. Here, the molecule might have a larger excited-state dipole moment (μ_e) than its ground state (μ_g) because of a redistributed charge separation under excitation (i.e., intramolecular charge transfer, ICT). This leads to a lowering in the excited state energy of the molecule due to the rotationally re-oriented solvent molecules surrounding it (i.e., dipole-dipole interaction) (59). This reduction in the excited state energy paves the way for a decrease in the energy gap between the ground state and the excited state, which results in a redshift in the fluorescence emission profile of the molecule.

To better understand the effect of the medium polarity on the photophysical properties of the pyrazoline derivatives, we also calculated their fluorescence quantum yields (FL-QYs) in 1,4-dioxane, too. The comparative results for the mediums having different polarity (i.e., toluene and 1,4-dioxane) are given in

Figure 4.11 as a bar graph. In the first group of samples (PyOx-1 – PyOx-3), a slight increase was observed in the FL-QYs in 1,4-dioxane compared to that in toluene. However, despite the increase, the FL QYs of the samples are still around 1%. On the other hand, it was found that certain samples exhibited a strong solvent polarity dependency in their FL-QYs. For instance, as can be seen in Figure 4.11, there is an almost 84% decrease in the FL-QYs of the group of samples, PyOx-4 to PyOx-6, comprising the -NO₂ group, with increasing solvent polarity. In the case of the -CN group at position 3 instead of the -NO₂ group, i.e., PyOx-7, the ratio of the decrease in the FL-QY with the increase in polarity of the solvent is slowing down (i.e., about 10%). In general, this significant reduction in FL-QY clearly displays the solvent polarity-dependent emission properties of the pyrazoline derivatives, which reveals the change in the rates of radiative and non-radiative decay processes in the emission mechanism (144). The dipole-dipole interactions between the solute with ICT characteristics and the solvent become generally stronger with increasing solvent polarity, which feeds the nonradiative decay processes and gives rise to a decrease in the FL QY(145–147).

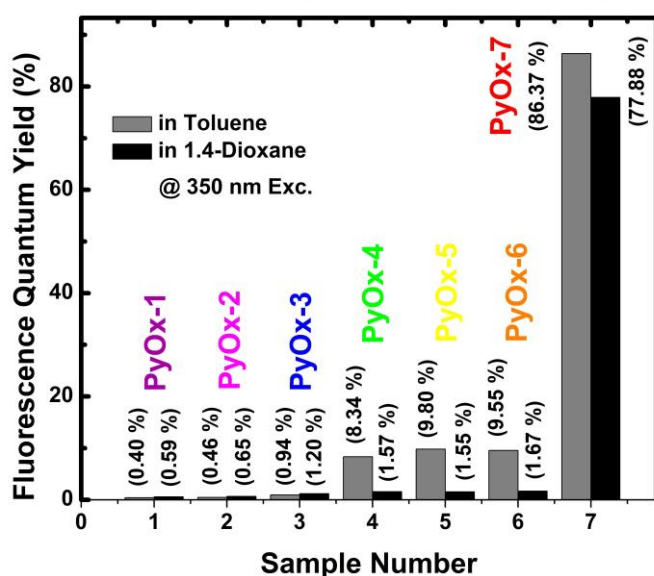


Figure 4.11. Comparative representation of the relative quantum yields of the pyrazoline derivatives both in toluene (gray bars) and 1,4-dioxane (black bars) for 350 nm excitation.

To deeply analyze the influence of solvent polarity on the photophysical properties of the synthesized compounds, we repeated absorption and fluorescence measurements for seven solvents having different polarity. To this end, we chose the PyOx-7 as a target compound due to its high FL-QY and relatively less red-shifted emission properties with an increase in the solvent polarity. In addition, during the measurements, the solvents having less to high polarity parameters $E_T(30)$ between 33 and 46 kcal/mol, toluene to dimethyl sulfoxide (DMSO), was used as host medium.

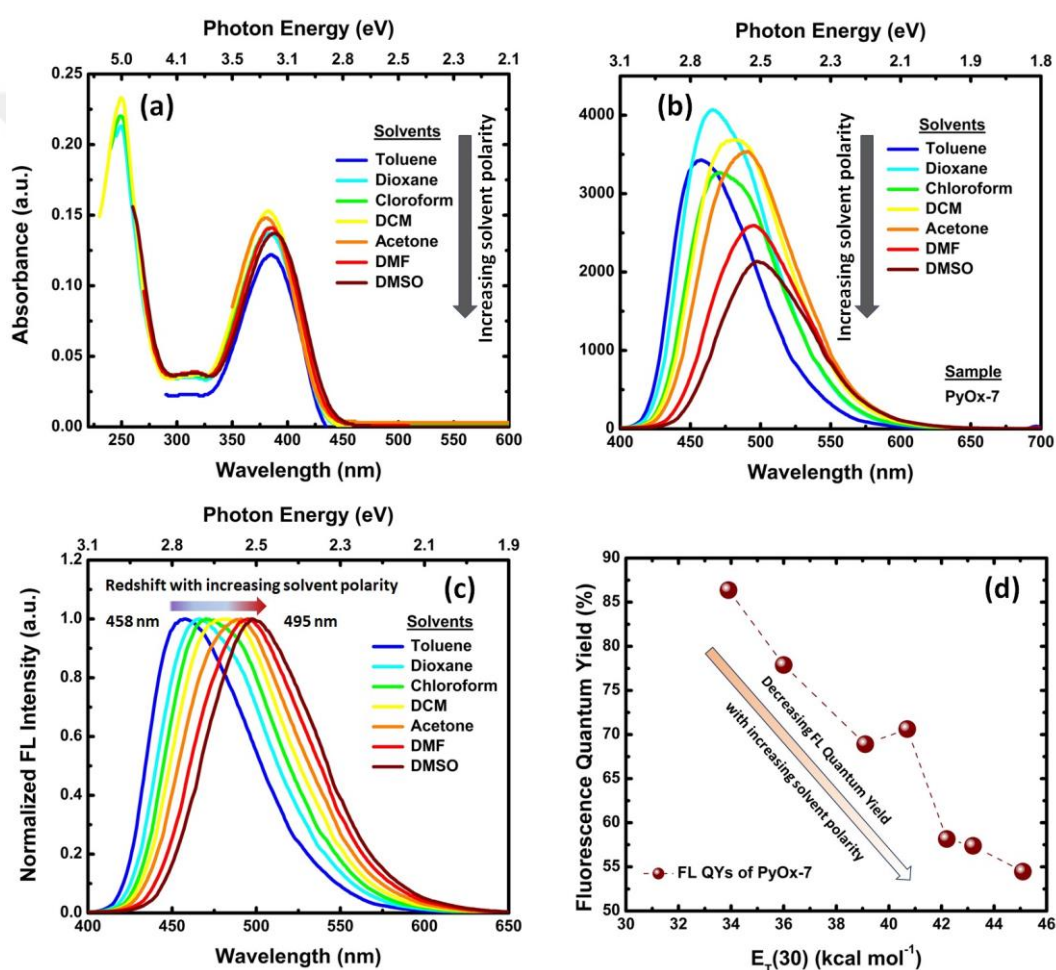


Figure 4.12. (a) UV-Vis absorption curves, (b)-(c) fluorescence and normalized fluorescence curves, and (d) relative fluorescence quantum yield of the pyrazoline derivatives for seven solvents having different polarities. Here, $E_T(30)$ given in (d) is the polarity parameter for the corresponding solvent (148).

Figure 4.12a shows the evolution of the absorption features of PyOx-7 with increasing solvent polarity. In the graph, the absorption curves were plotted in the spectral range of 220 to 600 nm. However, some curves were not given in the full spectra due to the specific absorption cut-off wavelength of the corresponding solvents. This specific wavelength is the point where all photons are absorbed; therefore, the wavelength below it was not shown. As can be seen in Figure 4.12a, generally, two main absorption peaks have emerged in the absorption spectrum. The first maximum is located on the short-wavelength side of the spectrum at about 250 nm, while the second absorption peak is positioned at about 385 nm. We observed a nearly solvent polarity-independent behavior. In other words, the general absorption profile remains almost unchanged and its spectral position shifts slightly with a few nanometers, which implies that no dramatic change in the ground state properties of the PyOx-7 with increasing solvent polarity.

In the case of the fluorescence measurements, in contrast to its absorption profile, a strong solvent-polarity-dependent behavior was observed. Figures 4.12b and 4.12c depict the steady-state fluorescence emission curves of PyOx-7 in seven solvents having different polarities. It was found that the fluorescence emission is shifted regularly to the longer-wavelength side of the spectrum with increasing solvent polarity. The emission peak emerged at 458 nm in a nonpolar solvent (i.e., toluene), whereas it is at 495 nm in a polar solvent (i.e., DMSO). In addition, this strong polarity-dependent behavior was also observed in the FL-QY of PyOx-7. The evolution of the FL-QY as a function of the solvent polarity scale (i.e., $E_T(30)$) is given in Figure 4.12d. It is clearly seen that the FL-QY is in a decreasing trend with increasing solvent polarity. It was found that the quantum yield of the emission is reduced from 86.4 to 54.5% with increasing polarity of the solvent. As we discussed in detail above, all these findings reveal that the emission mechanism of the compound is mainly governed by its ICT character, and the non-radiative decay pathways become more prominent with increasing solvent polarity.

4.3.3 Pyrazoline Derivatives in Solid State

Organic molecules that can exhibit fluorescence emission both in solution and solid phases are important for materials science and applied research. Understanding the photophysical properties of these molecules in their dilute solution is crucial to identifying their potential for applications in various fields, such as chemo-sensors and bio-imaging. However, it's equally important to investigate their emission properties in the solid state to gain insights into the impact of intermolecular interactions on their fluorescence properties, which is essential for optimizing the performance of organic materials in technologies like LEDs, and other optoelectronic devices. Therefore, we also studied the solid state photophysical properties of pyrazoline derivatives, which were examined within the scope of our thesis.

Figure 4.13 depicts the photos of the pyrazoline derivatives in solid state (i.e. powder form) under daylight (left column) and the excitation of the laser pointer with 405 nm wavelength (right column). It was observed that all samples exhibit solid state fluorescence emission from blue to red under excitation at room temperature. In addition to this rough observation, to determine whether the synthesized molecules have a solid-state emission, the steady-state photoluminescence (PL) measurements were carried out at room temperature to investigate the photophysical properties of these samples. Figure 4.14 presents the individual PL emission curves of all pyrazoline derivatives under 350 nm excitation. The measurements show that the first group of samples emits bluish-emission between 447 and 484 nm (i.e., PyOx-1 – PyOx-3), whereas the samples in the second group (i.e., PyOx-4 – PyOx-6) have a PL emission located between 533 and 600 nm (i.e., from green to red). This highly redshifted emission profile of the molecules comprising the nitro group at position 3 can be attributed to the strong electron-withdrawing nature of the nitro group (i.e., NO₂). In contrast to the findings based on the fluorescence measurements in solution, it was found that the substituents on the oxadiazole ring at position 5 significantly contribute to the emission properties of the pyrazoline derivatives in solid state.

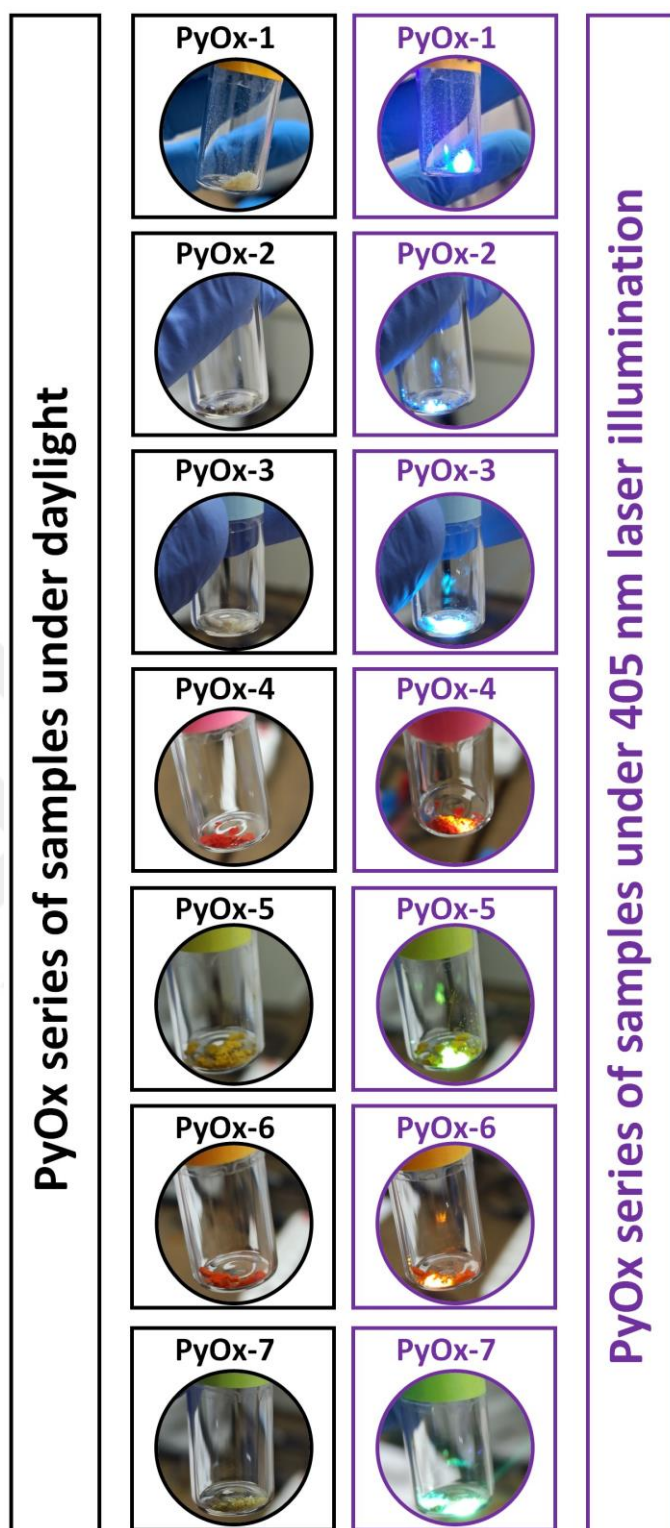


Figure 4.13. Photos of the solid state emissive pyrazoline derivatives under daylight (left column) and under 405 nm excitation by a hand laser (right column).

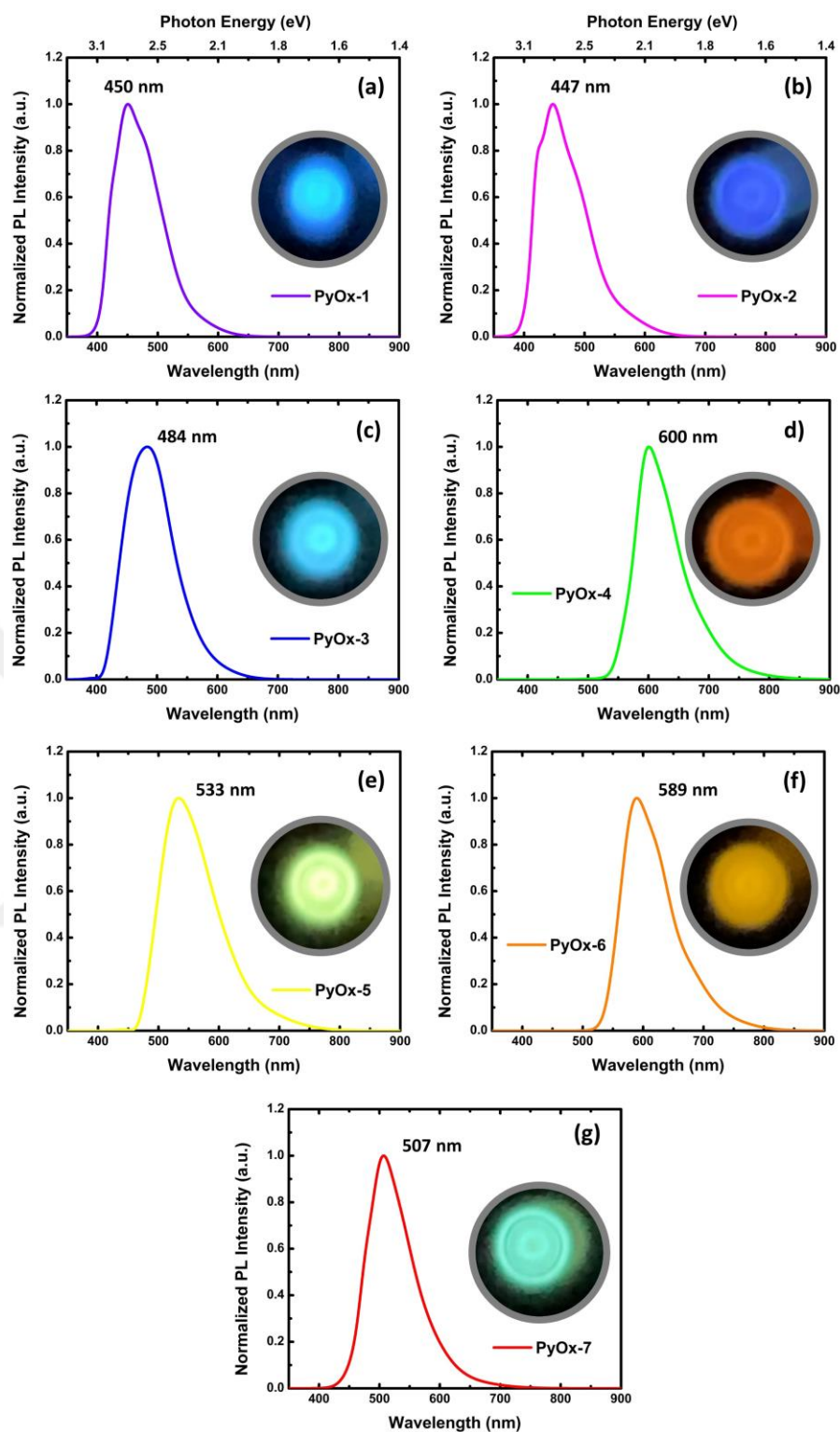


Figure 4.14. Normalized steady-state photoluminescence (PL) curves of the pyrazoline derivatives in solid-state under 350 nm excitation at room temperature. The insets show real-time photos of the excited samples during the measurements.

As can be seen in Figures 4.14 and 4.15a, depending on the substituent attached to the electron-withdrawing oxadiazole ring, the peak position of the PL curve shifts about 34 nm to the longer wavelength side of the spectrum in the first group compounds (i.e., PyOx-1 - PyOx-3). In the case of the compounds in the second group (i.e., PyOx-4 - PyOx-6), the amount of spectral shift in the PL maximum becomes more pronounced and reaches about 67 nm with the contribution of the highly electronegative NO₂ group. In addition, the critical importance of the electron-withdrawing ability of the substituent at position 3 in spectrally tuning the solid-state PL emission in these compounds is evident in the sample PyOx-7. The PL peak position appears at about 533 nm for PyOx-5, while at about 507 nm for PyOx-7. This blue-shifted behavior in the PL emission is due to the replacement of the strong electron-withdrawing nitro-group in PyOx-5 with the cyano-group having a relatively less electronegative nature. The shift in the spectral position of the PL emission to the longer wavelengths points out to reduction in energy gap between HOMO and LUMO. In molecule systems comprising electron donor and acceptor groups, generally, the electron-withdrawing groups reduce the energy gap between HOMO and LUMO by lowering the LUMO levels, whereas the electron-donating groups give rise to the same by raising the HOMO levels. The stronger electron-donating group leads to a greater increase in the HOMO level, while the stronger electron-withdrawing group paves the way for a greater decrease in the LUMO level (149–154). Therefore, the spectral shift in the peak position of the PL emission is directly related to the type (i.e., electron donor or acceptor) and electron-donating and accepting ability (i.e., weak or strong) of the substituents.

To better analyze the solid state photophysical properties of the synthesized pyrazoline derivatives, we also performed the measurements of their photoluminescence quantum yields (PL QYs). Figure 4.15b depicts the absolute PL QYs of the pyrazoline derivatives. The measurements show that the sample PyOx-1 has 18.2 % PL QY, which is the highest among all in the solid phase under 350 nm excitation. In the first group of samples, the PL QY is decreased by an amount of 66 and 75 % by introducing the -F and -OCH₃ group, respectively, instead of -Cl on the 1,2,4-oxadiazole ring at position 5. In the presence of the -Cl and -NO₂ at positions 1 and 3, respectively, the PL QYs of the compounds in the range of 5 %

to 7 %. On the other hand, the PL QY exhibits an increasing behavior of about 2.5-folds as the -NO₂ group at position 3 (i.e., PyOx-5) is replaced with the -CN group (i.e., PyOx-7). This increase in PL QY might be attributed to the relatively less electronegative nature of the -CN group compared to that of the -NO₂ group. Due to the highly electronegative nature of the -NO₂ group, the withdrawal of electron density from the system can destabilize the excited state, which increases the probability of non-radiative decay via inter-system crossing (ISC) or internal conversion (IC) and results in the fluorescence quantum yield decrease (155,156).

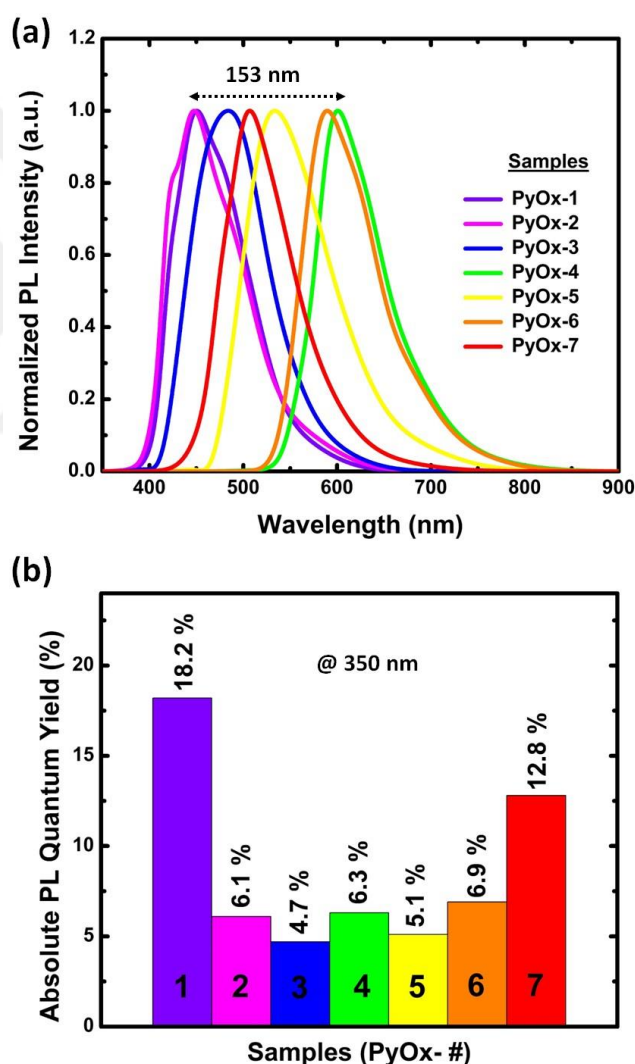


Figure 4.15. (a) Comparative representation of normalized photoluminescence curves, and (b) absolute photoluminescence quantum yields (PL-QYs) of the synthesized pyrazoline derivatives under 350 nm excitation.

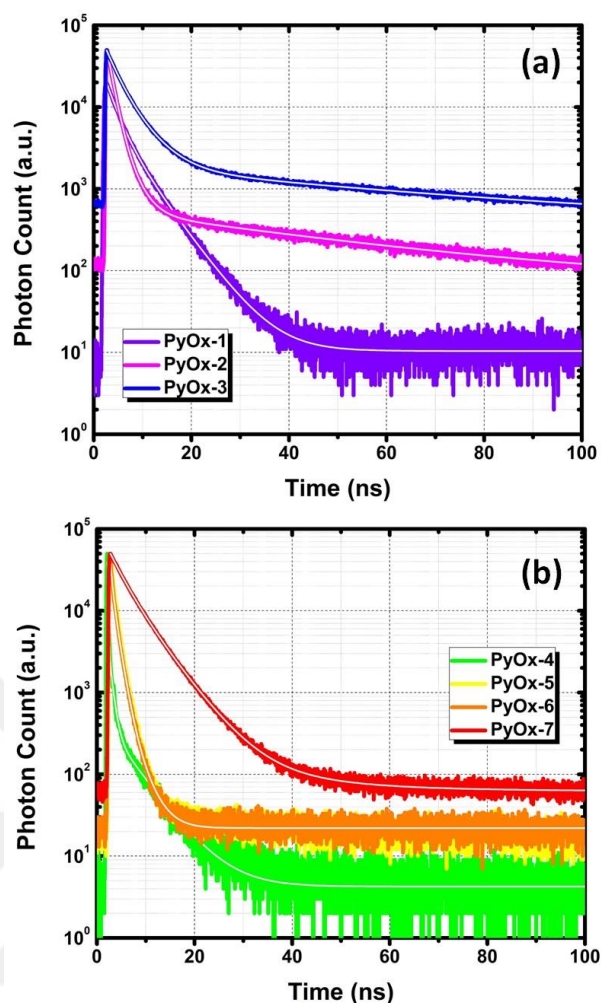


Figure 4.16. Time-resolved fluorescence (TRF) decay curves of (a) the first group compounds, PyOx-1 to PyOx-3, and (b) the second and third groups of compounds, PyOx-4 to PyOx-7, for their solid-state emissions. The white solid lines on the decay curves show the fitting curves.

On the other hand, time-resolved fluorescence (TRF) measurements were also carried out to gain an insight into the emission kinetics of the pyrazoline derivatives in solid state. Figure 4.16 shows the fluorescence decay curves of the pyrazoline derivatives in the solid state, which is collected at the maximum PL emission wavelength and room temperature by using the time-correlated single photon counting system and picosecond pulsed-pump laser having 375 nm of excitation wavelength. As can be seen from Figure 4.16a, the PL decay curve of the PyOx-2 is faster than those of the PyOx-1 and PyOx-3. In addition, it was observed that the decays of the PyOx-2 and PyOx-3 were not completed within 100 ns, which is an indication of a new decay channel with a long lifetime. This incomplete decay

within a given time frame may be associated with thermally activated delayed fluorescence (TADF). On the other hand, it has been observed that, in the case of the second group of samples, the PL decay curve is more accelerated with the introduction of the nitro group at position 3 of the pyrazoline ring as compared to those in the first group (see Figure 4.16b). In addition, it was found that the PL decay curve is elongated as the strong electron-withdrawing -NO₂ group is replaced with the relatively less electronegative -CN group (see PL decay curves of PyOx-4 and PyOx-7).

Furthermore, all decay curves were numerically fitted by utilizing the multiple-exponential decay function given below (58).

$$I(t) = \sum_{i=1}^n A_i e^{-\frac{t}{\tau_i}} \quad (4.1)$$

Here, I , t , A and τ are the fluorescence intensity, time, amplitude of the exponential decay and the fluorescence lifetime, respectively. The amplitude weighted average PL lifetimes (τ_{av}) of the compounds in the first group, PyOx-1 to PyOx-3, were calculated to be 3.11, 1.85, and 5.37 ns, respectively. The PL decay curve of the PyOx-1 was fitted to two-exponential decay function (i.e., $\tau_1 = 5.33$ ns and $\tau_2 = 2.04$ ns), whereas it is three-exponential for the PyOx-2 (i.e., $\tau_1 = 2.62$ ns, $\tau_2 = 1.18$ ns, and $\tau_3 = 46.16$ ns) and PyOx-3 (i.e., $\tau_1 = 4.80$ ns, $\tau_2 = 2.32$ ns, and $\tau_3 = 62.72$ ns). In general, the non-radiative processes are faster than the radiative ones, thus, τ_1 and τ_2 can be associated with radiative and non-radiative processes, respectively. In addition, the third decay component (τ_3), which is longer than the others (τ_1 and τ_2), might be related to TADF. However, the fractional contribution ($A_i \times \tau_i$) of this longer component to the emission is found to be weak, e.g., 0.96 % for PyOx-2 and 3.27 % for PyOx-3, in comparison with the contribution of other components. This new non-dominant and poor radiative decay pathway can lead to a shortening in the room-temperature radiative decay lifetime (157), which results in a reduction in PL QY.

In the case of the second group of samples (i.e., PyOx-4 – PyOx-6), the decay curves were fitted to three-exponential decay function. It was found that the amplitude weighted average lifetime (τ_{av}) is shortening with the introducing the -

NO₂ group at position 3 of the pyrazoline ring. For PyOx-1, PyOx-2, and PyOx-3, the τ_{av} was determined to be 0.22, 0.85, and 0.74 ns, respectively. The shortening in the average lifetime reflects the strong electron-withdrawing nature of the nitro group promoting non-radiative decay pathways, which reduces the overall efficiency of the fluorescence process. The decay components were calculated as $\tau_1 = 5.43$ ns, $\tau_2 = 0.73$ ns, $\tau_3 = 0.11$ ns for PyOx-4, $\tau_1 = 8.55$ ns, $\tau_2 = 1.32$ ns, $\tau_3 = 0.51$ ns for PyOx-5, and $\tau_1 = 2.62$ ns, $\tau_2 = 1.06$ ns, $\tau_3 = 0.35$ ns for PyOx-6. Here, two fastest decay components (i.e., τ_2 and τ_3) were attributed to the non-radiative processes and the component in the sub-nanosecond might be related to a newly opened non-radiative decay pathway due to the substitution of the -NO₂ group to the structure. This non-radiative process dominant emission kinetics leads to low PL QY for the nitro-substituted compounds, which explains why the samples in the second group exhibit low PL QYs.

On the other hand, the PL decay curve of the PyOx-7 was fitted to the three-exponential decay function, too. As we analyze the PL decay curve of the PyOx-7 comprising the cyano group instead of the nitro group compared to the PyOx-5, it has been found to have an elongated average PL lifetime ($\tau_{av} = 4.17$ ns). The decay components were calculated as $\tau_1 = 5.34$ ns, $\tau_2 = 2.63$ ns, and $\tau_3 = 17.65$ ns for PyOx-7, in which τ_1 and τ_2 might be associated with radiative and non-radiative processes, respectively. Like in those of the PyOx-2 and PyOx-3, the PL decay is looking incomplete within 100 ns, therefore the longest component τ_3 may be related to TADF. However, the fractional contribution of this component to the emission is highly low (0.48 %). It was also found that the fractional contribution of τ_1 is increased with the cyano group, whereas it is in a decreasing trend for τ_2 . This suppressed non-radiative process gives rise to an enhancement in the fluorescence emission, which is well consistent with the PL QY results.

To better understand the emission kinetics of the compound in terms of the radiative and non-radiative processes, we have also calculated the radiative and non-radiative decay rates utilizing the results in the absolute PL QYs and the average PL lifetime measurements. To this end, the following equation was used,

$$k_r = \frac{\Phi_{PL}}{\tau} \quad (4.2)$$

and

$$k_{nr} = \frac{[1-\Phi_{PL}]}{\tau} \quad (4.3)$$

where, k_r and k_{nr} are the radiative and nonradiative decay rate constants, Φ_{PL} and τ are PL QY and PL lifetime, respectively. Figure 4.17 depicts the calculated radiative and nonradiative decay rate constants of the pyrazoline derivatives in the solid state. As can be seen from Figure 4.17b, the radiative decay rate decreases when the -Cl atom as a substituent on the 1,2,4-oxadiazole ring (PyOx-1) is replaced with the -F atom (PyOx-2). The decrease might be explained by the size of the Cl and F atoms. The atomic size of the F atom is smaller than the Cl atom, leading to an enhancement in molecular packing and intermolecular interactions, particularly in the context of π -stacking. This also gives rise to an increase in the non-radiative decay rate, resulting in decreasing PL QY (see Figures 4.15b and 4.17a). On the other hand, in the case of PyOx-3, the radiative decay rate is still in the decreasing trend, but the non-radiative decay rate is also decreasing in contrast to that in PyOx-1 and PyOx-2. The -OCH₃ group in the PyOx-3 has a large molecular volume as compared to the halogens in the PyOx-1 and PyOx-2. This leads to a decrease in the molecular packing promoting the radiative decay processes, and it is expected that an increase in PL QY, like in that of the PyOx-1. However, the PL QY of the PyOx-3 is the lowest in the first group samples. This points out another factor to decrease the radiative decay rate. The most important factor that stands out here is the strong electron-donating ability of the -OCH₃ group. The 1,2,4-oxadiazole ring and the halogens on this ring have an electron-withdrawing nature in PyOx-1 and PyOx-2. In the case of PyOx-3, the strong electron-donating ability of the -OCH₃ group can reduce the electron-withdrawing nature of the oxadiazole ring. Thus, the presence of the methoxy group may induce intramolecular effects, such as changes in molecular conformation and electronic structure. Although strong electron-donating groups generally tend to enhance fluorescence, intramolecular effects can influence the excited-state dynamics, potentially leading to a decrease in the radiative decay processes. Figure 4.17c shows the ratio between the non-radiative decay rate and the radiative decay rate. The results reveal that the non-radiative decay processes are respectively about 4- and 5-fold more dominant in the overall

emission mechanism of the PyOx-2 and PyOx-3 than in the PyOx-1, which is consistent with the PL QY results.

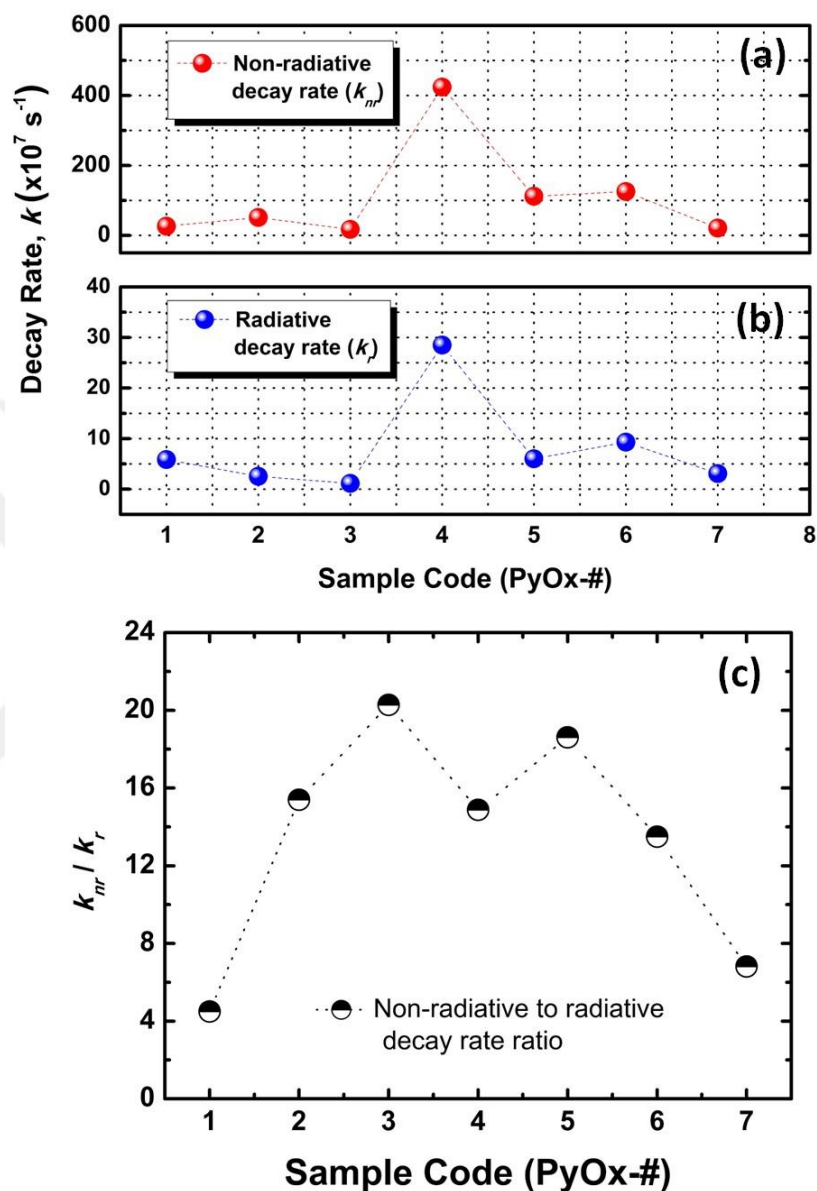


Figure 4.17. The calculated (a) non-radiative and (b) radiative decay rates of the solid-state emissive pyrazoline derivatives. (c) The ratio of the non-radiative decay rate to the radiative decay rate.

Furthermore, it was found that both radiative and non-radiative decay rates are enhanced in the second group samples by attaching the -Cl at position 1 and the -NO₂ at position 3 of the pyrazoline ring compared to those of the samples in the first group. However, it is obviously seen that the strong electronegative nature of

the nitro group promotes the non-radiative decay processes. As can be seen Figure 4.17c, the ratio between the non-radiative and the radiative decay rates (k_{nr}/k_r) is high in the range between 14 and 19. Therefore, the PL QYs of this group of samples are poor due to highly non-radiative decay processes dominated emission mechanism. On the other hand, the decay rate results reveal that the cyano group at position 3 tends to reduce both radiative and non-radiative decay rates compared to the PyOx-7 with the PyOx-5 (see Figure 4.17a and 4.17b). However, the reduction in the non-radiative decay rate is about 2.5-fold higher than the decrease in the radiative decay rate. The emission mechanism including suppressed non-radiative decay processes, due to the relatively less electron-withdrawing -CN group, gives rise to an enhanced PL emission behavior, in other words, promoting the higher PL QY.

4.3.4 Color-Conversion LED Application

Due to all synthesized pyrazoline derivatives exhibiting solid-state emission properties, we have also performed their proof-of-concept demonstration as color-conversion materials in LED applications. To this end, first, we prepared monolithic samples of the pyrazoline derivatives using potassium bromide (KBr) salt. To prepare pyrazoline monoliths, about 5 μ mol samples in powder form were ground with 450 mg of dried KBr salts for about 15 min using an agate mortar. The ground pyrazoline/KBr powders were pressed under 80 kN force. Figure 4.18 depicts the photographs of the prepared monoliths with and without pyrazoline derivatives under daylight and UV light with 405 nm. It is seen from the figure that all monoliths with the pyrazoline derivatives exhibit fluorescence emission under 405 nm UV light excitation although KBr-only monoliths do not.

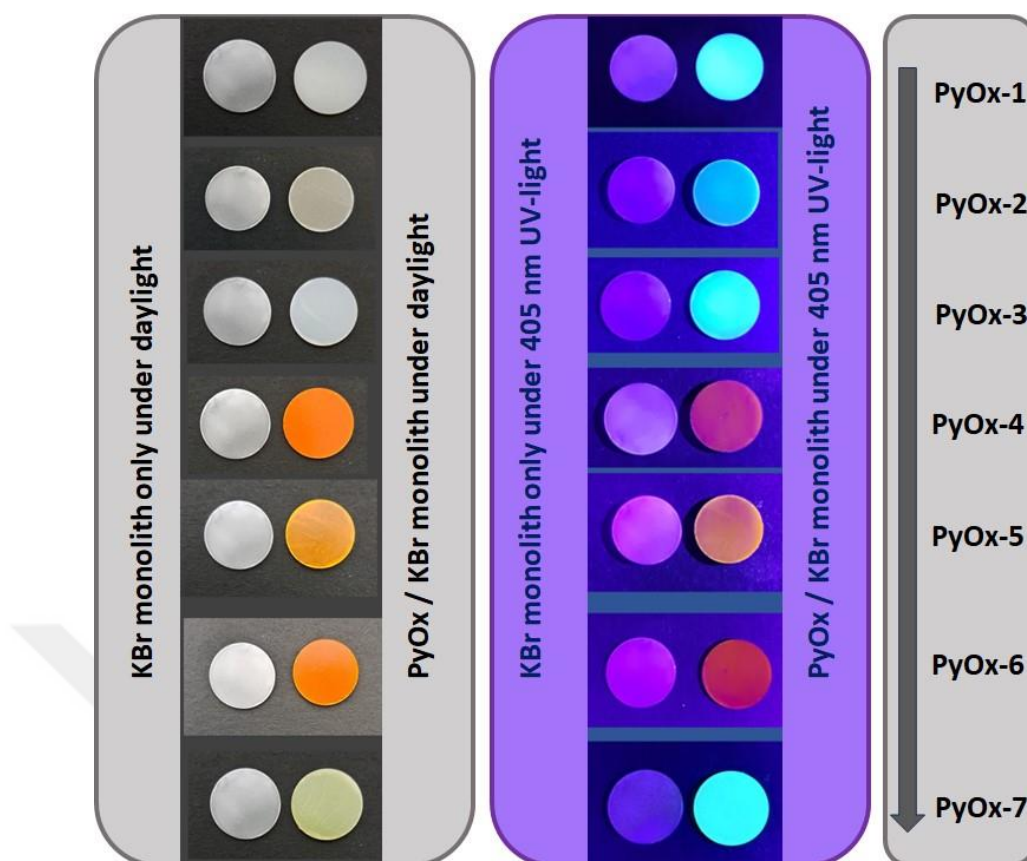


Figure 4.18. The photos of prepared KBr-only and PyOx/KBr monoliths under daylight (left column) and 405 nm of UV light (right column).

To perform the color converted LED application, the prepared PyOx/KrBr monoliths were employed on a high-power near-UV-LED chip that emits at 405 nm. Figure 4.19 shows the photos of the PyOx/KBr monolith integrated LEDs and their CIE color coordinate (x,y) diagram. It was found that the wavelength of the LED, which is in the near-UV region of the spectrum, was successfully converted to the wavelength corresponding to the region of blue, green, and red. With the first group of samples (i.e., PyOx-1 – PyOx-3), it was obtained the blue-LEDs, whereas the red-LEDs resulted using the second group samples (i.e., PyOx-4 – PyOx-7). In addition, using the PyOX-7 resulted in obtaining a green-LED. The CIE color coordinates of the color-converted LEDs, which are calculated by analyzing the PL emission spectrum of the monolith coupled with the UV-LED chip, also confirm the conversion of the emission wavelength of the UV-LED chip to longer wavelengths.

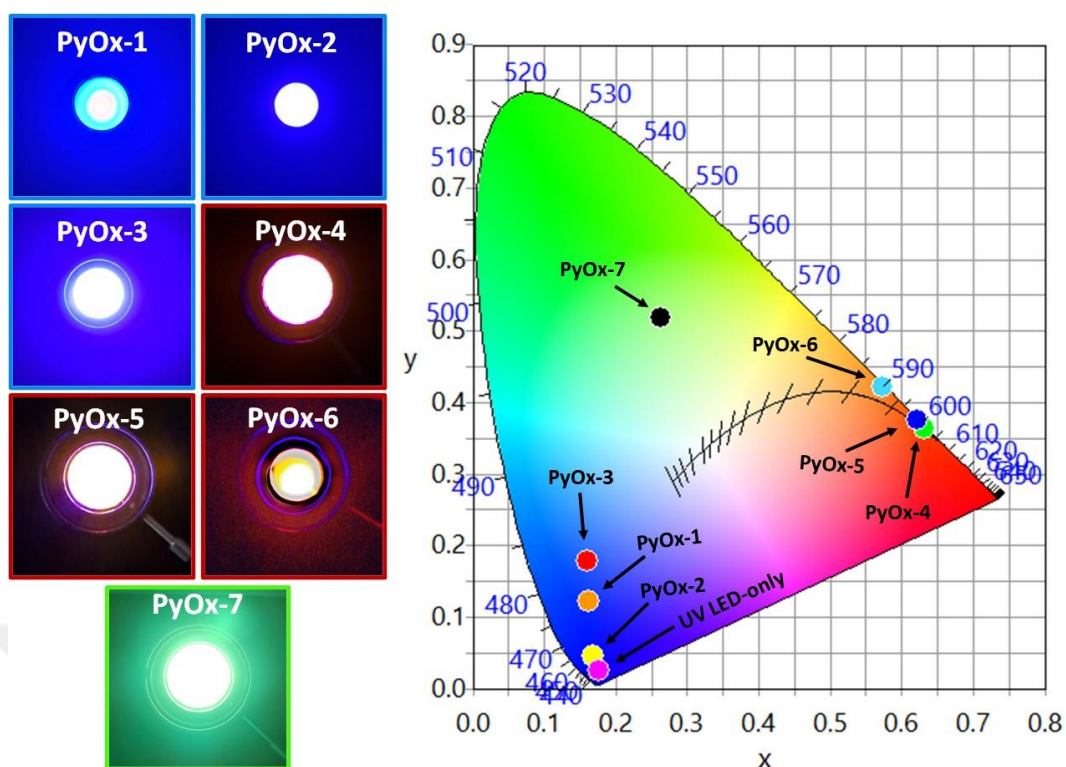


Figure 4.19. The photographs of the PyOx/KBr monolith integrated near-UV LED chips for color-conversion application, and their CIE color coordinate diagram.

On the other hand, it was observed that the PL spectrum of the samples in a monolithic structure comprising the nitro group at position 3 of the pyrazoline ring exhibits redshifted behavior compared to the spectra collected for their powder form. Figure 4.20 shows the PL spectrum of the prepared PyOx/KBr monoliths including pyrazoline derivatives comprising the nitro and cyano groups. As can be seen from the figure, the PL peak positions of the monolithic PyOx-4, PyOx-5, and PyOx-6, which include the nitro group, are located at 614, 603, and 618 nm, respectively. However, it has emerged at 600, 533, and 589 nm for the powder forms of the PyOx-4, PyOx-5, and PyOx-6, respectively (see Figure 4.14). The highest redshift under the mechanical stress is found to be 70 nm for the PyOx-5. This redshifted behavior in PL emission profile owing to the external mechanical effect (i.e., pressing under 80 kN) reveals that the PyOx series comprising -NO₂ group shows a typical mechano-fluorochromic (MFC) property. To better understand this effect, the PL spectrum of the monolith PyOx-7 was also examined. Here, the main difference between the PyOx-5 and PyOx-7 is that the PyOx-7 contains a cyano group instead of the nitro group in its structure, unlike the PyOx-

5. The PL spectrum of the monolith PyOx-7 has shown that no shift was found in the PL peak position after experiencing the external force.

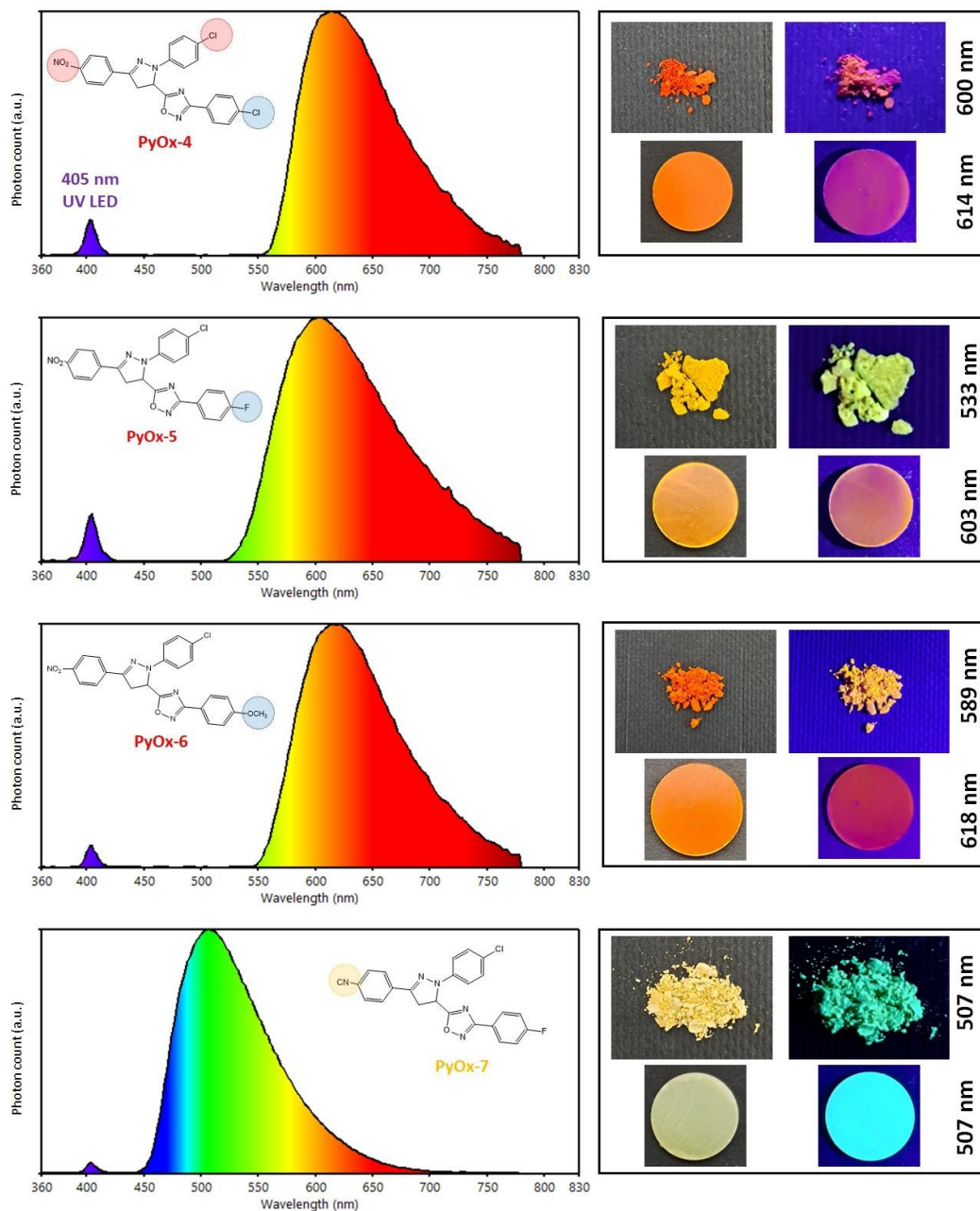


Figure 4.20. The PL spectrum of the prepared monoliths comprising the pyrazoline derivative having the nitro and the cyano groups. In the right column, the photos of pyrazoline derivatives in powder and pellet forms under daylight and 405 nm UV light. The maximum emission wavelengths of samples both in powder and pellet forms are also given near the photos.

The comparison of the PL spectra of the monolith and powder PyOx-7 has shown that no shift (i.e., 507 nm) was found in the PL peak position after experiencing the external force, which reveals that the -NO₂ group promotes the change in the fluorescence emission characteristics of our samples under the external mechanical effects. This redshifted behavior in the PL spectrum by the mechanical stimuli can be explained with the possible changes in the molecular packing, intermolecular interactions, and electronic structure (158,159).



5. CONCLUSIONS AND RECOMMENDATIONS

The results of the current dissertation study may be summarized as follows:

In the first section of the current study, five *C,N*-diaryl substituted hydrazone chlorides **1a-e** and three aryl substituted vinyl-1,2,4-oxadiazoles **2a-c** were produced as the precursor compounds, and their structures were supported by using IR and NMR data from the literature. Then, 7 novel 1,3-disubstituted-5-(1,2,4-oxadiazolyl) pyrazolines **3a-g** (i.e., PyOx-1 – PyOx-7) were synthesized in good-excellent yields by reacting in situ generated nitrilimines aryl vinyl-1,2,4-oxadiazoles (**2**) under basic conditions. The structure of 1,2,4-oxadiazole-pyrazoline hybrid compounds PyOx-1 – PyOx-7 was identified by physical (m.p., Rf) and spectral data (IR, ¹H-NMR, ¹³C-NMR, HRMS). As the result of cycloaddition reactions, only C-5 regioisomers of pyrazolines PyOx-1 – PyOx-7 have been seen to form regarding NMR data.

Due to the synthesized pyrazoline derivatives exhibiting fluorescence emission both in solution and solid state, in the second section, their photophysical properties were studied using spectroscopic techniques such as UV-Vis absorption and, steady-state and time-resolved fluorescence. The UV-Vis absorption measurements in their dilute solutions revealed that the absorption features of the 1,2,4-oxadiazole-pyrazoline hybrid compounds were not significantly affected by the substituents on the oxadiazole ring at position 5. However, it was also found dramatic changes in the absorption features depending on the electron-withdrawing ability of the substituent at position 3. In addition, steady-state fluorescence measurements for their dilute solution in toluene showed that the fluorescence properties of the samples in terms of the spectral position and quantum yield are highly affected by the substituent at position 3 of the pyrazoline ring. However, no significant contribution was found to the fluorescence properties by the substituents on the 1,2,4-oxadiazole group at position 5. For instance, it was found that the fluorescence emission shifts to longer wavelengths with increasing electron-withdrawing ability of the substituent at position 3. Furthermore, the fluorescence quantum yield was enhanced with the strong electron-withdrawing groups at position 3. The fluorescence quantum yield in solution was found to be 86.4%,

which is the highest one, in the presence of the cyano group at position 3. On the other hand, the solvent polarity-dependent measurements have revealed that all compounds have solvatochromic characteristics. It was found that the FL emission is shifted regularly to longer wavelengths, although the general absorption profile remains almost unchanged with increasing solvent polarity. Besides, the FL quantum yield of the compounds is generally in a decreasing trend with increasing medium polarity. For the compound having the highest FL quantum yield in solution, it was found a reduction reaching about 37 % in the quantum yield with increasing solvent polarity. All these findings reveal that the pyrazoline derivatives have intramolecular charge transfer characteristics, and the non-radiative decay pathways become more dominant in their emission mechanisms with increasing solvent polarity.

The measurements also showed that all compounds exhibit photoluminescence emission, which covers the blue to red regions of the electromagnetic spectrum, in their solid forms. It was found that the substituents both on the aryl ring at position 3 and the oxadiazole ring at position 5 remarkably contribute to the solid-state emission features of the pyrazoline derivatives. The maximum shift in PL emission is found to be 153 nm from the blue to red region. In addition, it was found that all compounds exhibit low PL quantum yields in the solid state, in which the highest one is 18.2 %. The time-resolved fluorescence measurements have revealed that the non-radiative decay rate is at least 4-fold faster than the radiative one, which points out the non-radiative process dominated emission kinetics in the solid form of the compounds. The results are also consistent with the PL quantum yields in the solid state. On the other hand, it was also found that the prepared monolithic structures of the compounds comprising the nitro group for the color-conversion application exhibit highly mechano-fluorochromic characteristics, where PL emission shifted up to 70 nm to the longer-wavelength side of the spectrum. Moreover, as a proof-of-concept demonstration, the pyrazoline monoliths were used as a color-converter layer by employing them on the near-UV LED with 405 nm. The results showed that color of the LED was successfully converted to the blue, green, and red emissions using the pyrazoline derivatives.

6. REFERENCES

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7. APPENDICES

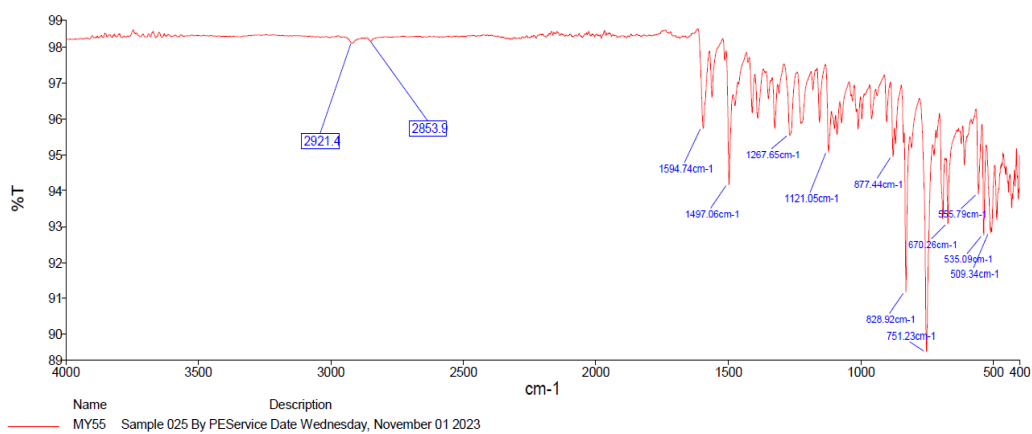


Figure 7.1. Infrared (IR) spectrum of **3a** (i.e., PyOx-1).

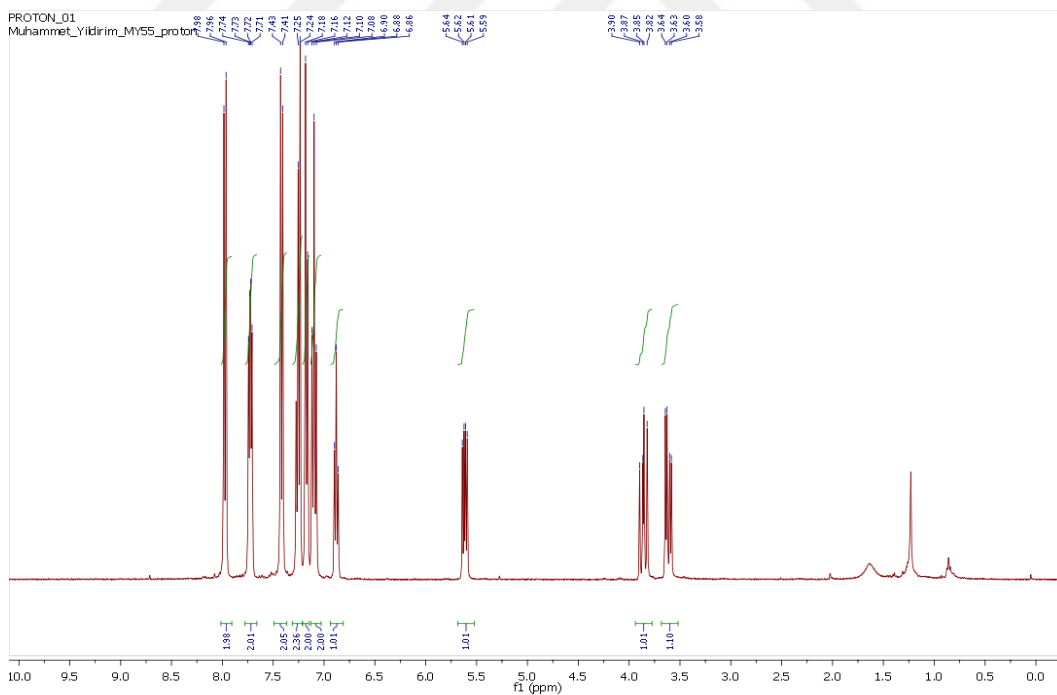


Figure 7.2. ¹H NMR spectrum of **3a** (i.e., PyOx-1).

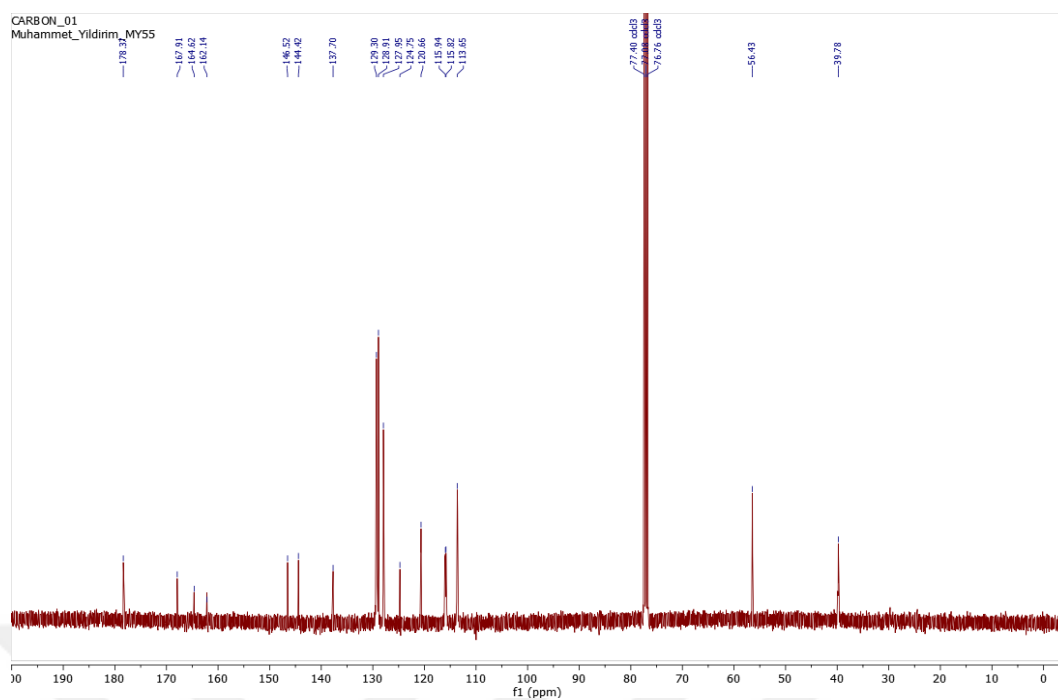


Figure 7.3. ^{13}C NMR spectrum of **3a** (i.e., PyOx-1).

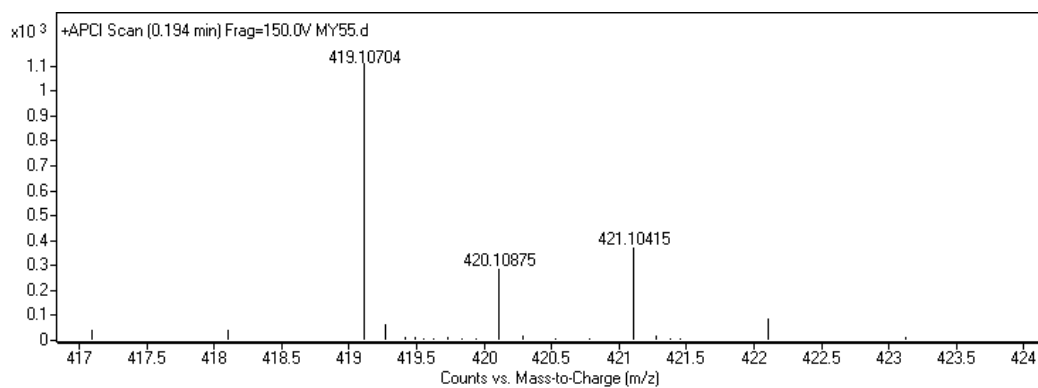


Figure 7.4. Time-of-flight mass spectrometry (TOF-MS) of **3a** (i.e., PyOx-1).

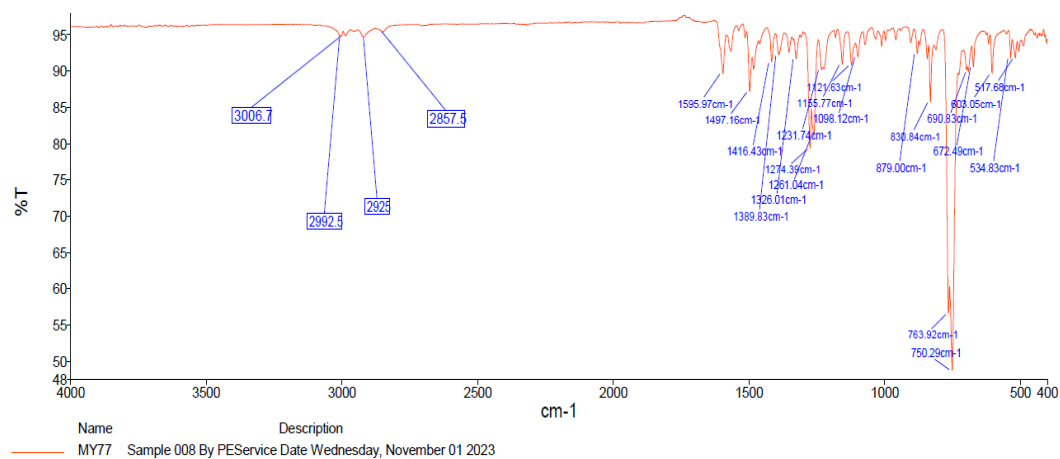


Figure 7.5. Infrared (IR) spectrum of **3b** (i.e., PyOx-2).

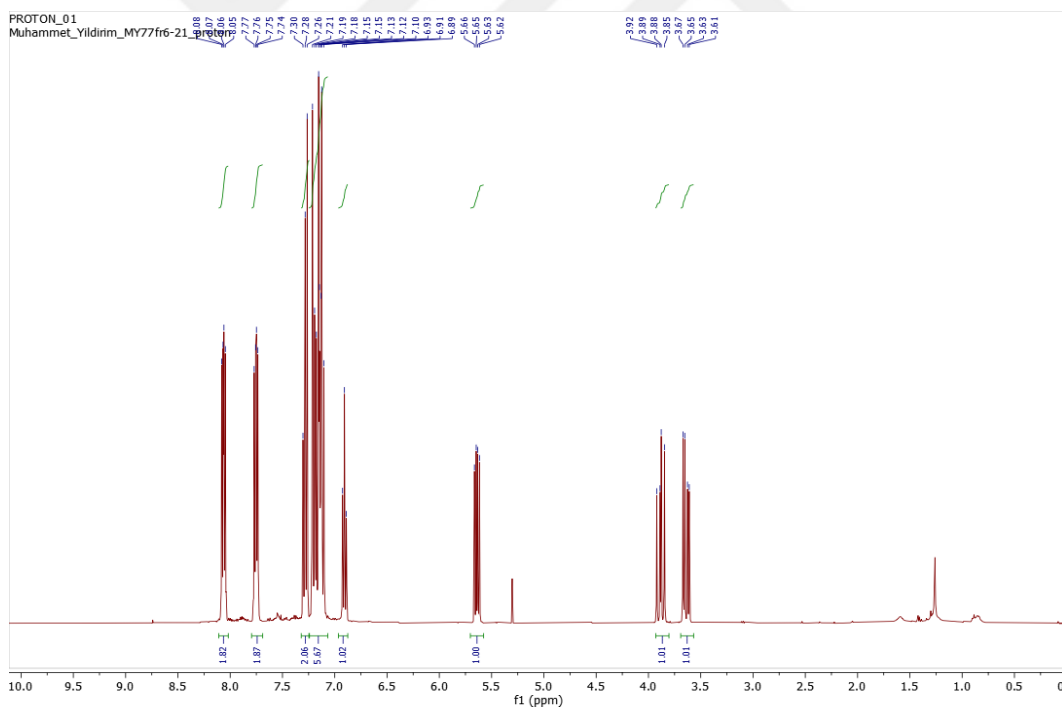


Figure 7.6. ¹H NMR spectrum of **3b** (i.e., PyOx-2).

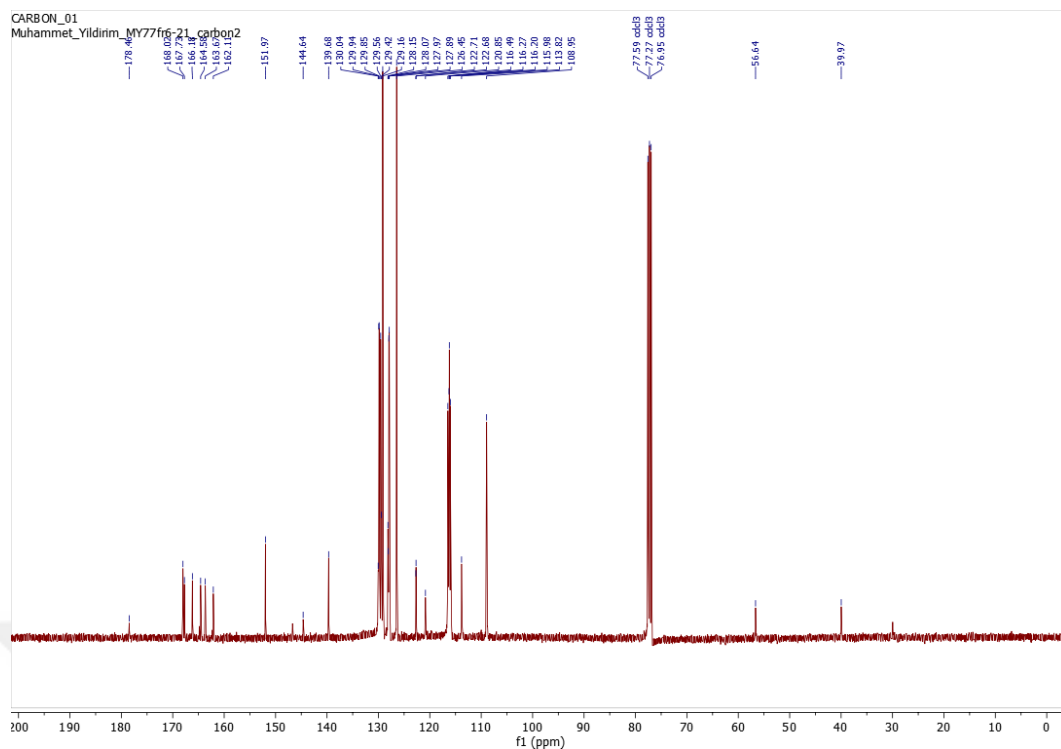


Figure 7.7. ^{13}C NMR spectrum of **3b** (i.e., PyOx-2).

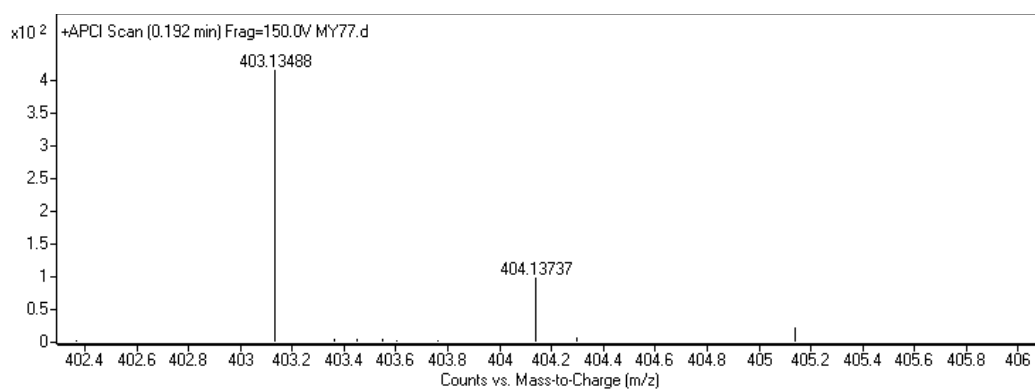


Figure 7.8. Time-of-flight mass spectrometry (TOF-MS) of **3b** (i.e., PyOx-2).

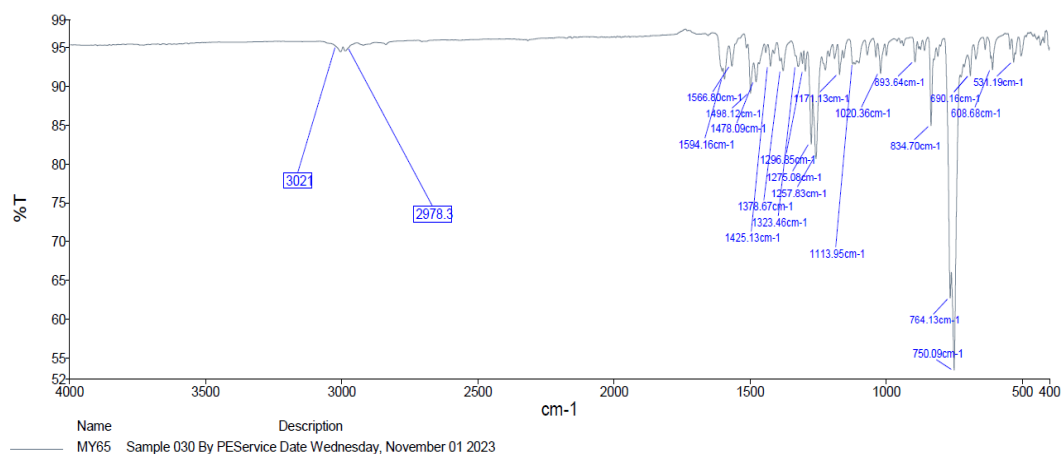


Figure 7.9. Infrared (IR) spectrum of **3c** (i.e., PyOx-3).

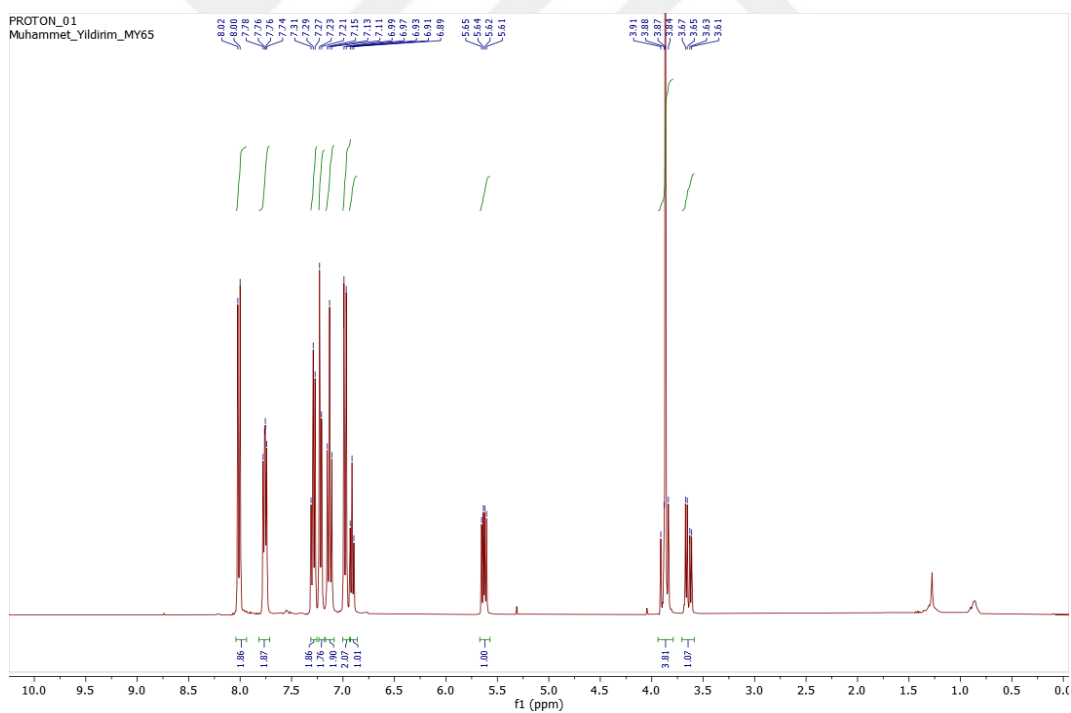


Figure 7.10. ^1H NMR spectrum of **3a** (i.e., PyOx-1).

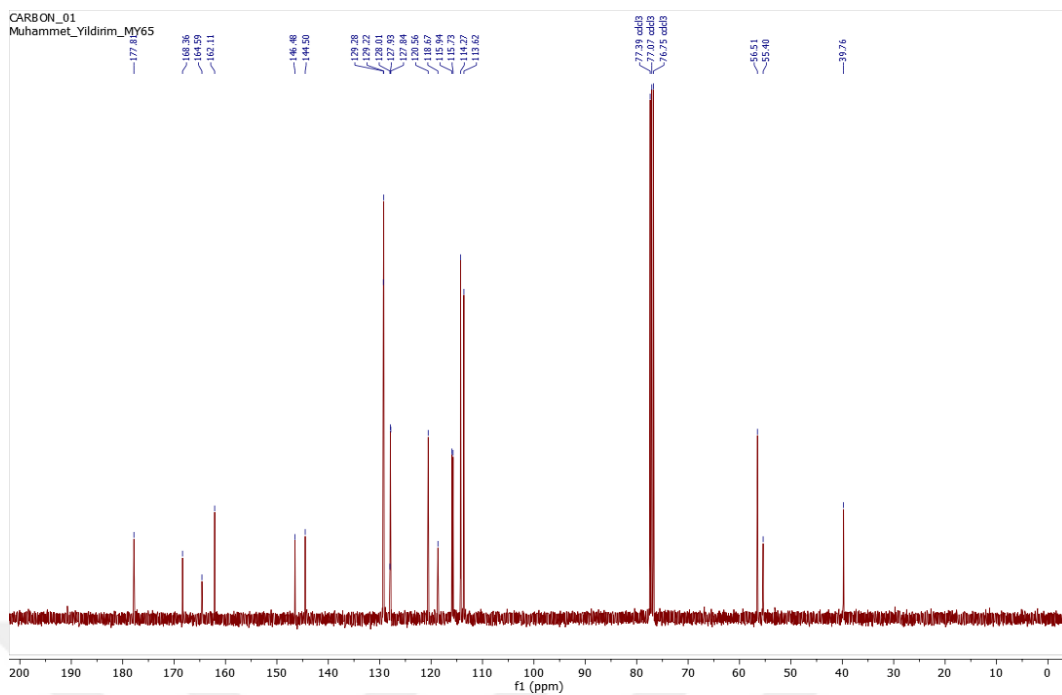


Figure 7.11. ^{13}C NMR spectrum of **3c** (i.e., PyOx-3).

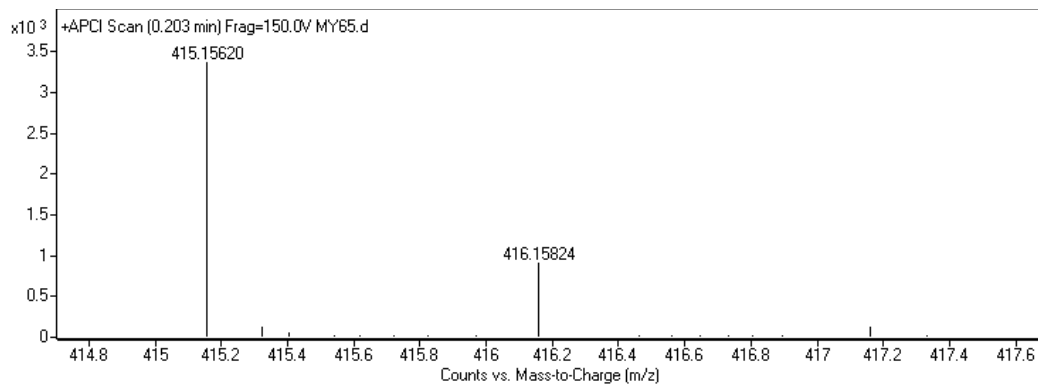


Figure 7.12. Time-of-flight mass spectrometry (TOF-MS) of **3c** (i.e., PyOx-3).

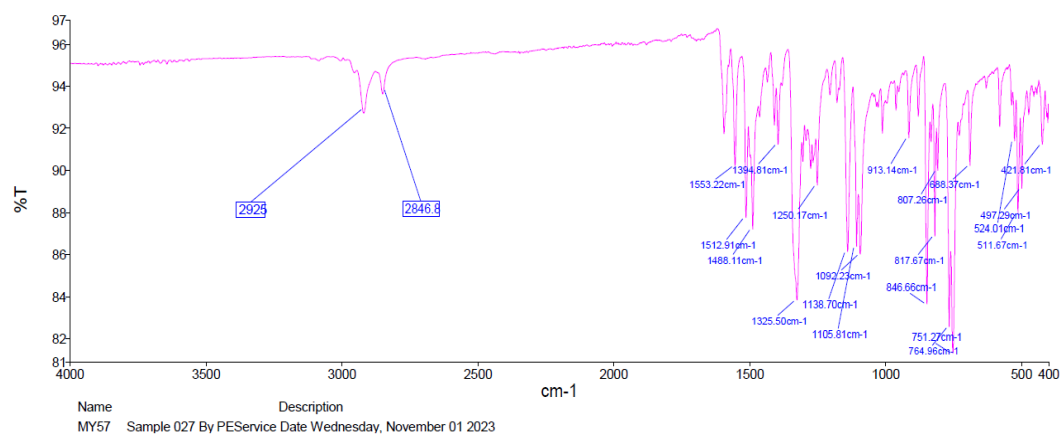


Figure 7.13. Infrared (IR) spectrum of **3d** (i.e., PyOx-4).

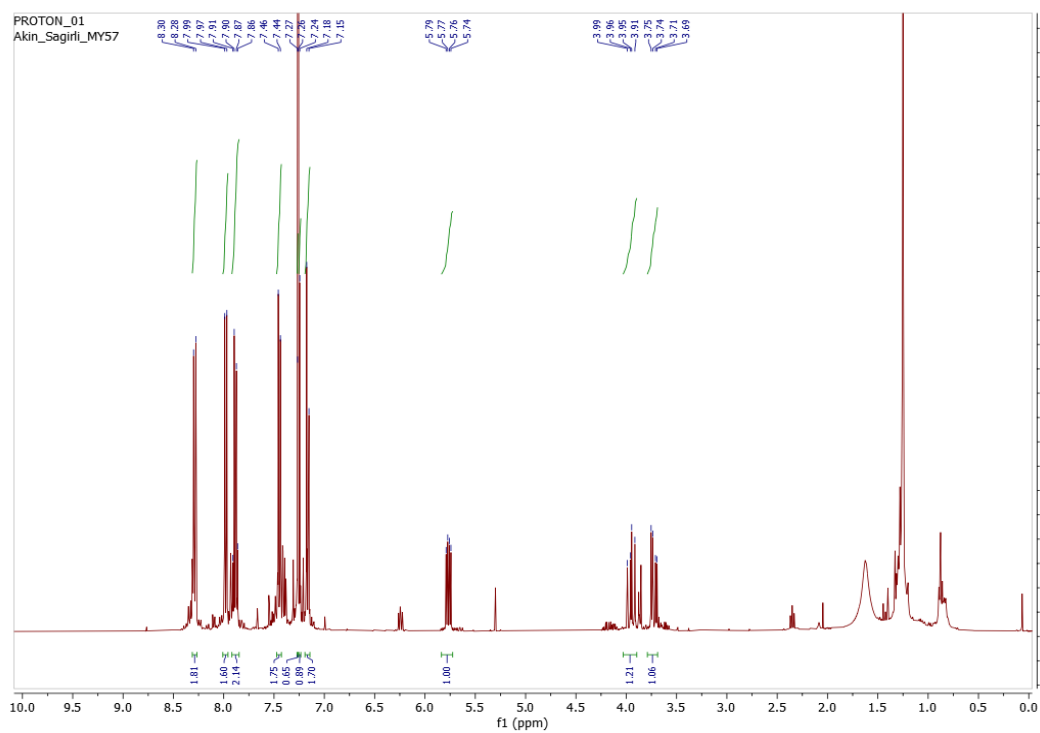


Figure 7.14. ¹H NMR spectrum of **3d** (i.e., PyOx-4).

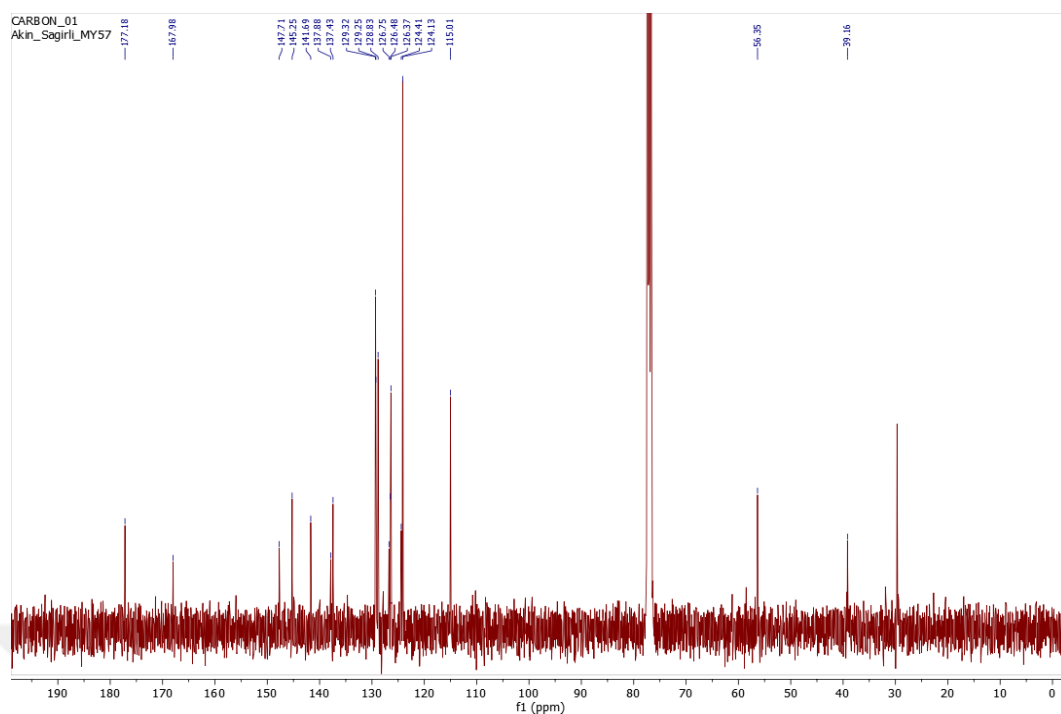


Figure 7.15. ^{13}C NMR spectrum of **3d** (i.e., PyOx-4).

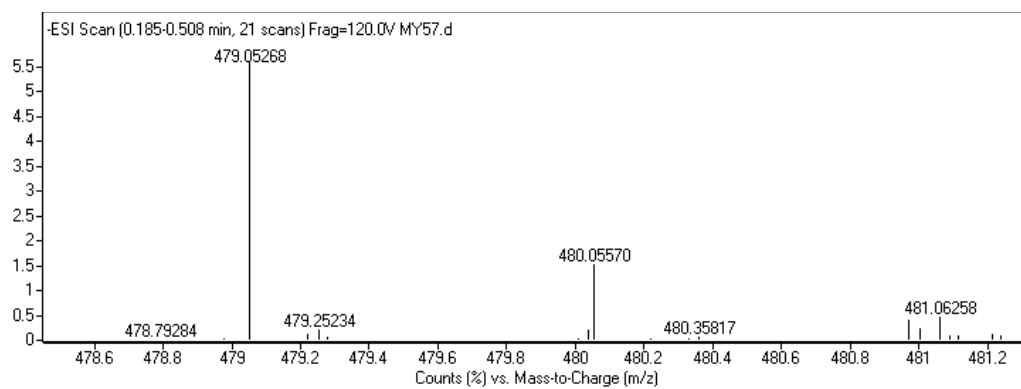


Figure 7.16. Time-of-flight mass spectrometry (TOF-MS) of **3d** (i.e., PyOx-4).

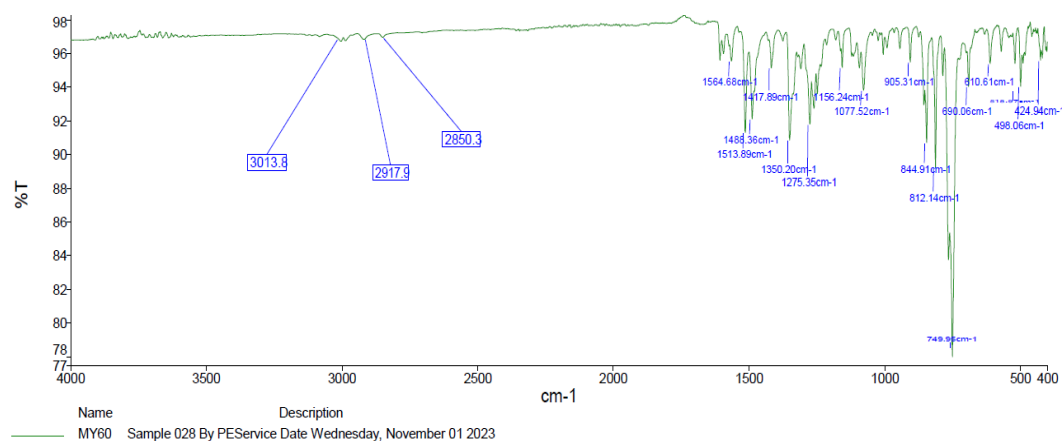


Figure 7.17. Infrared (IR) spectrum of **3e** (i.e., PyOx-5).

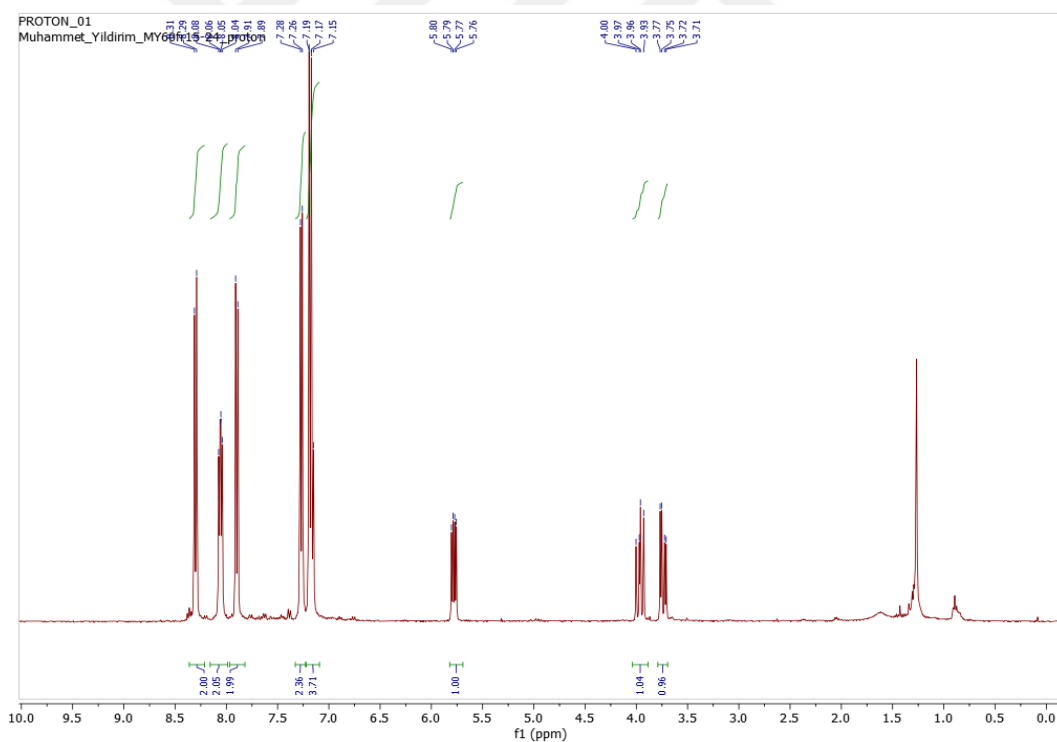


Figure 7.18. ^1H NMR spectrum of **3e** (i.e., PyOx-5).

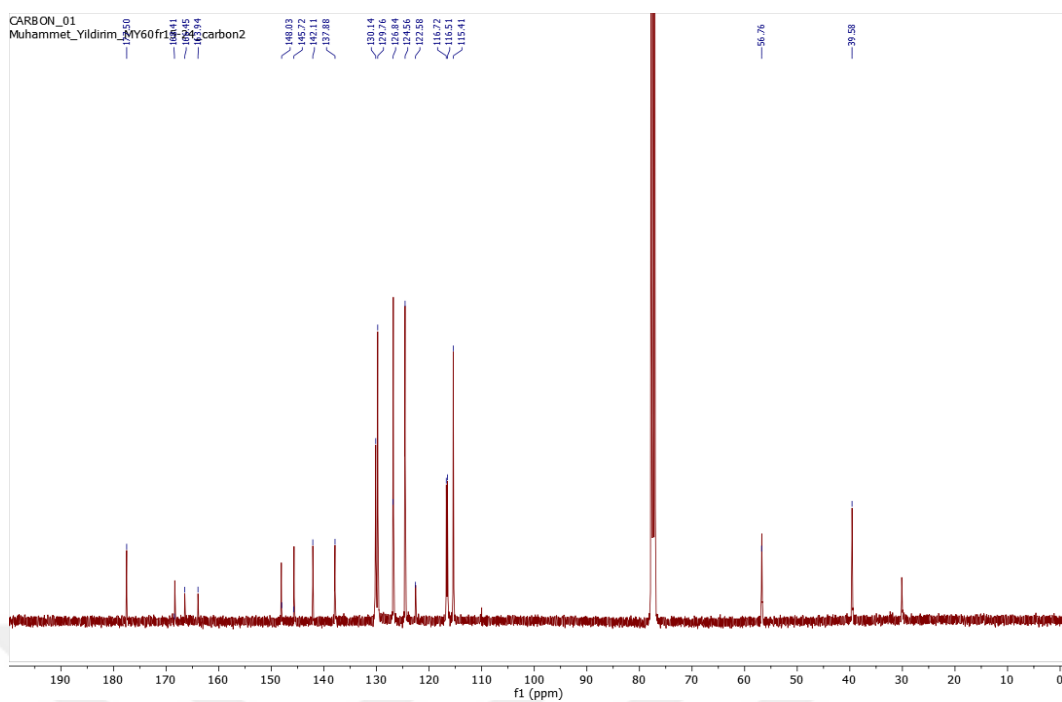


Figure 7.19. ^{13}C NMR spectrum of **3e** (i.e., PyOx-5).

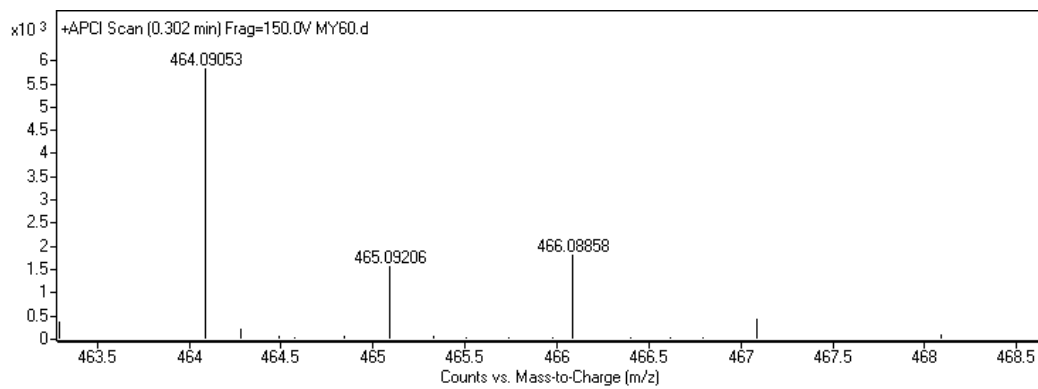


Figure 7.20. Time-of-flight mass spectrometry (TOF-MS) of **3e** (i.e., PyOx-5).

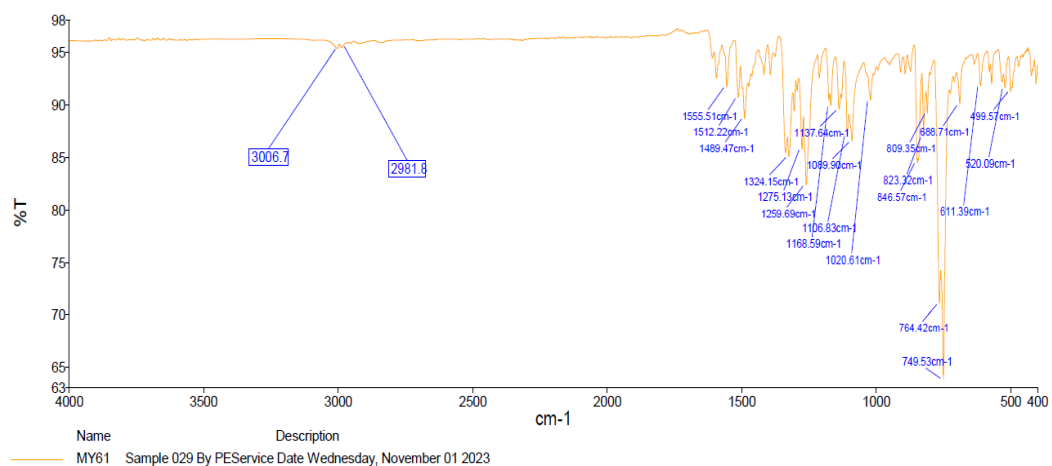


Figure 7.21. Infrared (IR) spectrum of **3f** (i.e., PyOx-6).

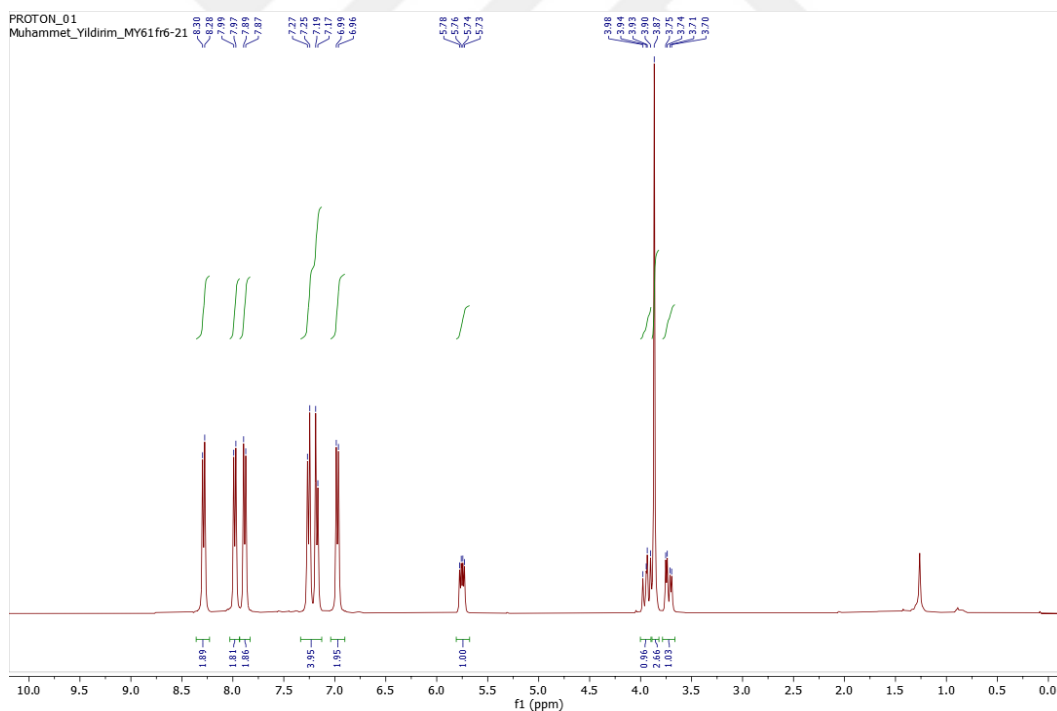


Figure 7.22. ¹H NMR spectrum of **3f** (i.e., PyOx-6).

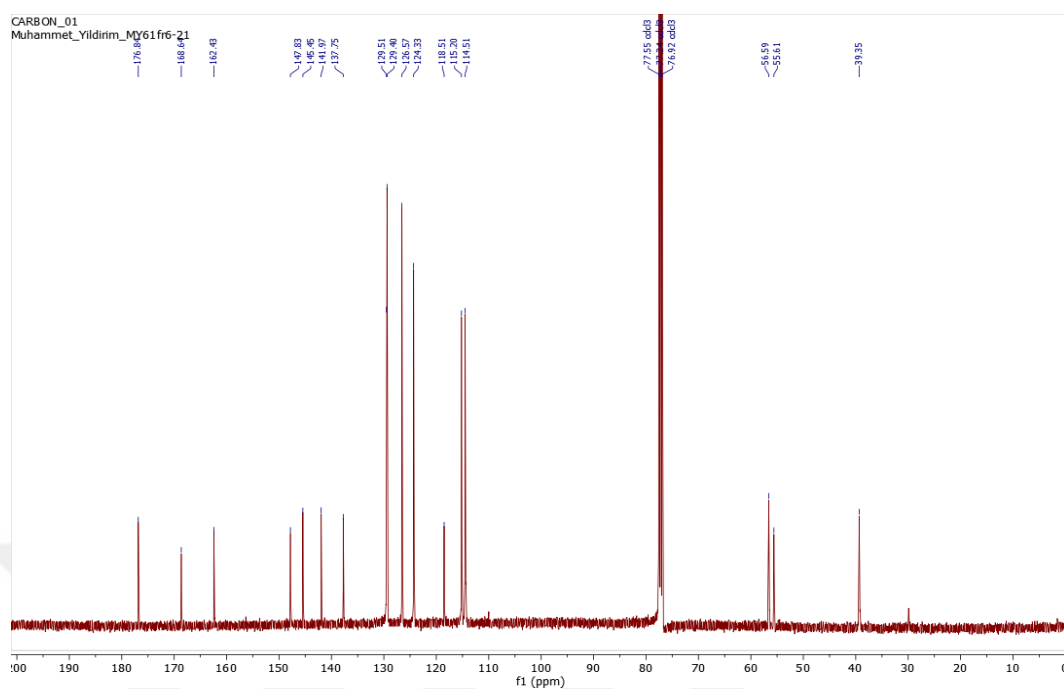


Figure 7.23. ^{13}C NMR spectrum of **3f** (i.e., PyOx-6).

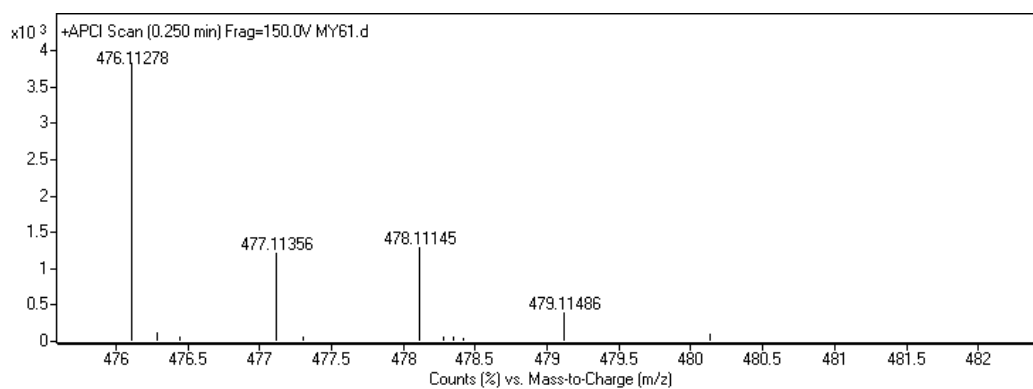


Figure 7.24. Time-of-flight mass spectrometry (TOF-MS) of **3f** (i.e., PyOx-6).

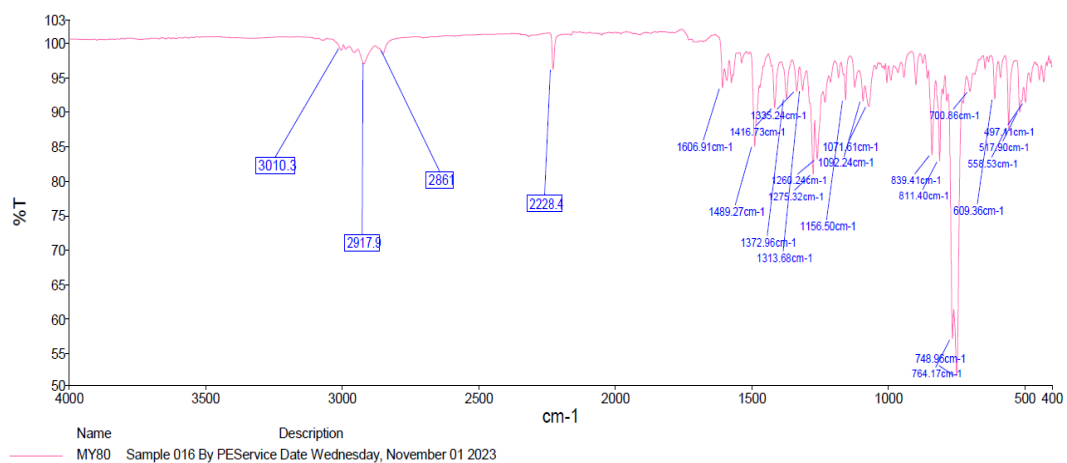


Figure 7.25. Infrared (IR) spectrum of **3g** (i.e., PyOx-7).

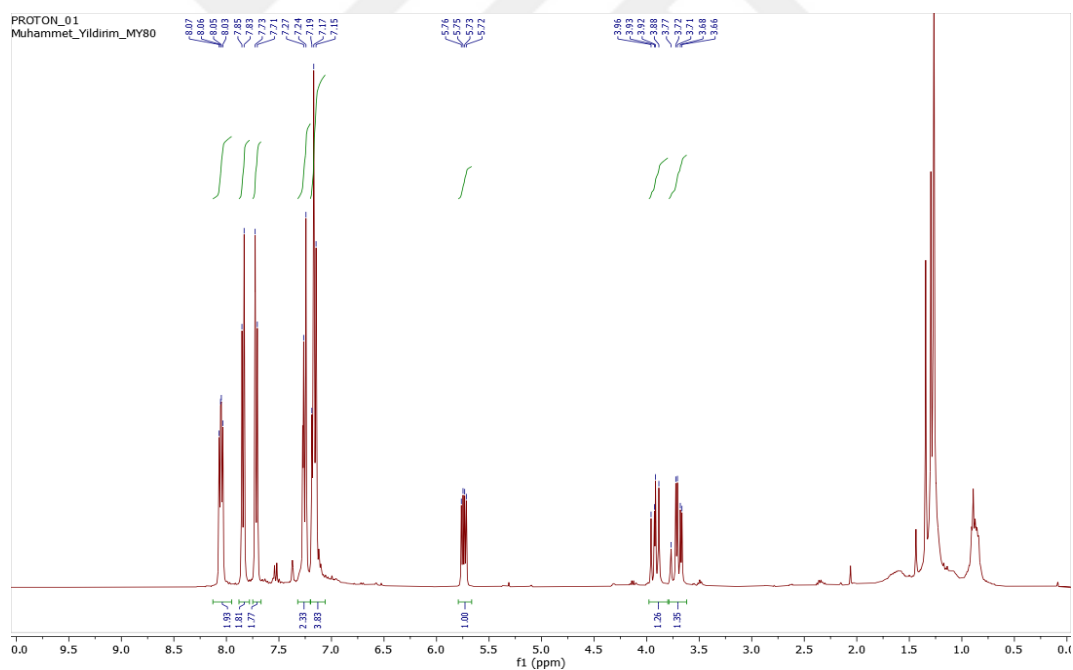


Figure 7.26. ¹H NMR spectrum of **3g** (i.e., PyOx-7).

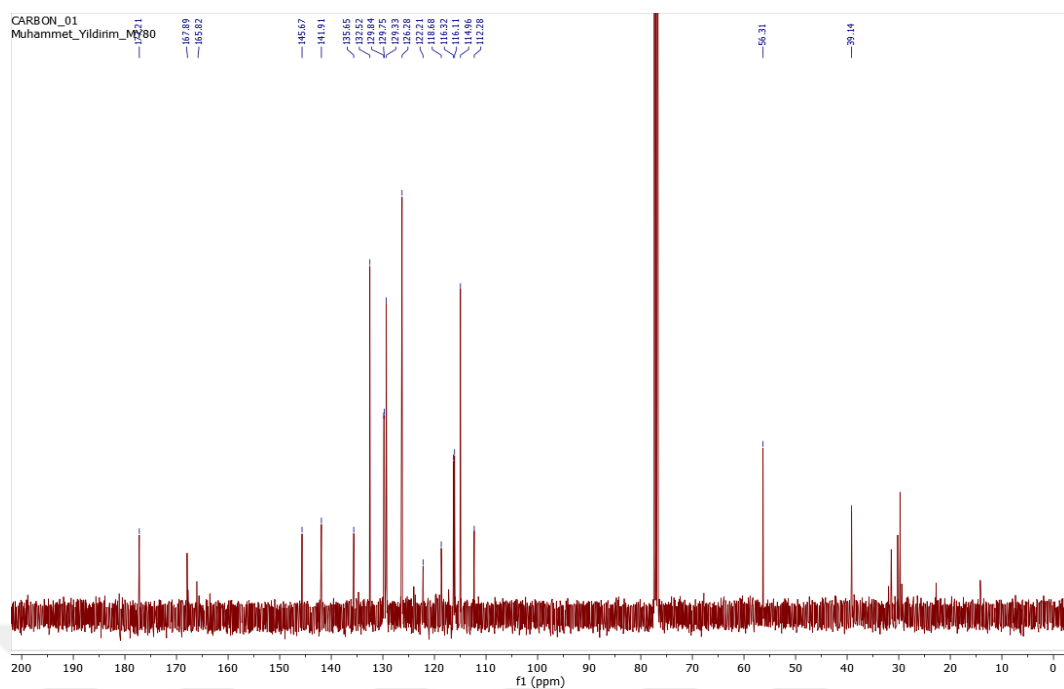


Figure 7.27. ^{13}C NMR spectrum of **3g** (i.e., PyOx-7).

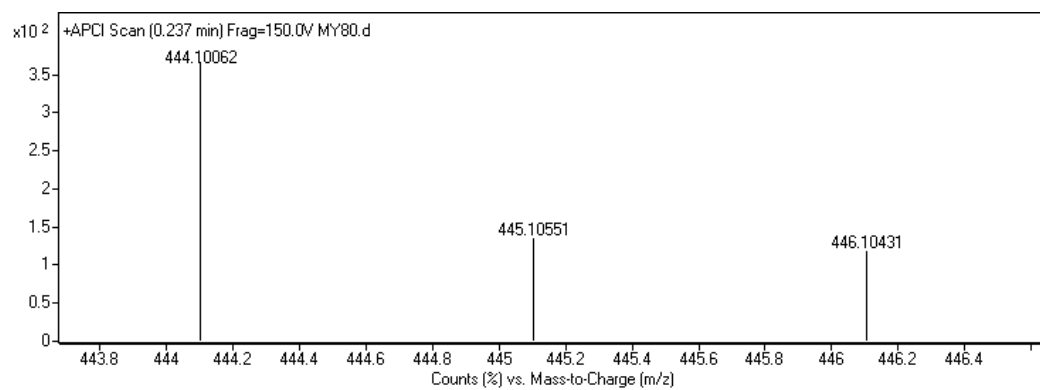


Figure 7.28. Time-of-flight mass spectrometry (TOF-MS) of **3g** (i.e., PyOx-7).