

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

FACILE SYNTHESIS OF FUNCTIONAL HYDROGEL SENSORS
VIA PHOTOCHEMICAL ROUTES

MUSTAFA UYGUN
A THESIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
DEPARTMENT OF CHEMISTRY

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PROF. DR. AYŞE GÜL GÜREK

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T.C.
GEBZE TEKNİK ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ

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GEBZE
2018

GTÜ Fen Bilimleri Enstitüsü Yönetim Kurulu'nun 24/10/2018 tarih ve 2018/53 sayılı kararıyla oluşturulan jüri tarafından 13/11/2018 tarihinde tez savunma sınavı yapılan Mustafa Uygun'un tez çalışması Kimya Anabilim Dalında DOKTORA tezi olarak kabul edilmiştir.

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SUMMARY

In this thesis study, acrylamide- N,N'-bisacrylamide based hydrogels were synthesized via photopolymerization technique using fluorescence active photoinitiators and sensing performance of formed gels were investigated against heavy metal ions and nitroaromatic compounds by using fluorescence spectroscopy. This study consist of two parts based on fluorophore groups of dansylchloride and cinacalcet hydrochloride.

In the first part, hydrogel containing dansyl flourophore was synthesized via photopolymerization of acrylamide- N,N'-bisacrylamide using danysl chloride as photoinitiator under UV irradiation in one-pot manner. Then sensing performance of formed sensor gel was examined against different metal cations and nitroaromatic compounds.

In the second part, same strategy and methodology was employed for the synthesis of cinacalcet functional hydrogel. Then sensing performance of formed sensor gel was examined against different metal cations and nitroaromatic compounds. Also for both compounds, initiation mechanism of photopolymerization were investigated using electron spin resonance spectroscopy and UV-visible spectroscopy.

Key Words: dansyl, cinacalcet, photoinitiation, heavy metal ion-sensing, nitroaromatic compound, hydrogel.

ÖZET

Bu tez çalışmasında floresan aktif fotobaşlatıcı kullanılarak fotopolimerizasyon yöntemi ile akrilamid/ N,N'-bisakrilamid esaslı hidrojel sentezlenmiş ve elde edilen jellerin sensör performansı, floresan spektroskopisi kullanılarak ağır metal iyonlarına ve nitroaromatik bileşiklere karşı araştırılmıştır. Bu çalışma florofor grupları dansil klorür ve sinakalset hidroklorüre dayalı olarak iki kısımdan oluşmaktadır.

Birinci bölümde, dansil florofor grubu içeren hidrojel, UV ışınlaması altında foto-başlatıcı olarak dansil klorür kullanılarak akrilamid- N, N'-bisakrilamidin fotopolimerizasyonu yoluyla tek basamakta sentezlendi. Sentezlenen jelin sensör performansı farklı metal katyonları ve nitroaromatik bileşiklere karşı incelendi.

İkinci kısımda, sinakalset fonksiyonel hidrojel sentezi için aynı strateji ve metod kullanılmıştır. Elde edilen jelin sensör performansı farklı metal katyonları ve nitroaromatik bileşiklere karşı incelendi. Her iki bileşik için de, fotopolimerizasyonun başlatma mekanizması elektron spin rezonans spektroskopisi ve UV-görünür bölge spektroskopisi kullanılarak araştırılmıştır.

Anahtar Kelimeler: dansil, sinakalset, foto-başlatma, ağır metal iyonu algılama, nitroaromatik bileşik, hidrojel.

ACKNOWLEDGEMENTS

I would like to express my sincere appreciation to people who have helped and supported me during my time in Gebze Technical University over the years: Special thanks to my advisor Prof. Dr. Ayşe Gül Gürek and Assoc. Prof. Dr. Mehmet Atilla Taşdelen for their valuable guidance and encouragement to finish my thesis; and Assoc. Prof. Dr. Erdinç Doğanç for his ongoing support.

I would also like to express my gratitude to Professors, Hayal Bülbül Sönmez and Nergis Arsu for serving on my committee and making valuable suggestions.

I owe a special thanks to Prof. Dr. Faruk Yılmaz for his guidance and contribution during the research. I would like to thank to Abdi İbrahim İlaç San. ve Tic. A.Ş. for support me during my Ph.D. education.

I would also like to thank my laboratory mates Enis Taşçı, Muhammet Aydın, Sümeyra Bayır, Ahmet Üner, Figen Aynalı, Zeynep Şahin for their friendship and for being ready whenever I needed them.

I would like to dedicate my thesis to my dearest father, mother, brothers and my dear spouse Gözde, their love patience, understanding and support over the years makes my life more meaningful and enjoyable.

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LIST of ABBREVIATIONS and ACRONYMS

<u>Abbreviations and Acronyms</u>	<u>Explanations</u>
1,2-DNB	: 1,2-Dinitrobenzene
2, 4-DNP	: 2, 4-Dinitrophenol
2, 4-DNT	: 2, 4-Dinitrotoluene
4-NP	: 4-Nitrophenol
4-NT	: 4-Nitrotoluene
λ_{ex}	: Excitation wavelength
ε	: Molar extinction coefficient
$\Phi_{\text{R.}}$	: Quantum yield of radical formation
Φ_{p}	: Quantum yield of photoinitiation
AAm	: Acrylamide
A	: Absorbance
ATR-FTIR	: Fourier transform infrared spectroscopy
BAAm	: N,N'-methylenebisacrylamide
BPO	: Benzoyl peroxide
C	: Concentration
Cd^{+2}	: Cadmium ions
CDCl_3	: Deuterated chloroform
Co^{+2}	: Cobalt ions
COI	: Coinitiator
Cu^{+2}	: Copper ions
E	: Excitation energy
eq.	: equivalent
f_{p}	: Initiation efficiency of photogenerated radicals
FTIR	: Fourier Transform Infrared Spectroscopy
g/mL	: gram/ milliliter
h	: Planck's constant
Hg^{+2}	: Mercury ions
$h\nu$	: Radiation

$^1\text{H-NMR}$	: Hydrogen Nuclear Magnetic Resonance Spectroscopy
k	: Rate constant
K_{sv}	: Stern-Volmer constant
l	: Light path length
mL	: milliliter
MMA	: Methyl methacrylate
Mn^{+2}	: Manganese ions
Ni^{2+}	: Nickel ions
nm	: Nanometer
PA	: Picric acid
PAAm	: Polyacrylamide hydrogel
Pb^{+2}	: Lead ions
PI	: Photoinitiator
PMMA	: Poly(methyl methacrylate)
PS	: Photosensitizer
$\text{R}\cdot$	: Radical
QE	: Quenching efficiency ratio
SEM	: Scanning electron microscope
Sn^{2+}	Tin ions
SR	: Swelling ratio
TNT	: Trinitrotoluene
UV	: Ultraviolet
W	: Watt
W_s	: Weight of equilibrium swollen gel
W_d	: Weight of dry gel
w/w	: Weight/ Weight
Zn^{+2}	: Zinc ions

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1. INTRODUCTION

Gels are three-dimensional polymeric networks assembled with physical forces or chemical bonds and has capability of incarcerate large amount of solvent molecules in their structures. The gel can be called as a hydrogel or an organogel depending on the nature of the liquid component; the water is for hydrogel and the organic solvent is for organogels.

Hydrogels are unique material class, which are composed of a self supporting, water swollen three-dimensional elastic network, and enable diffusion of analyte molecules and enhanced surface area for binding target analytes. Due to their three-dimensional hydrophilic polymer network structures, capable of swelling and retaining a significant amount of water in an aqueous solution or biological fluids, soft slippery surface properties when swollen state, hydrogels found wide application range such as artificial tissues and organs, drug release system, agriculture, contact lenses, analyte sensing, dyes and heavy metal ions removal [1-3].

Sensor molecules can be immobilize to hydrogel with high density, because of hydrogels have porous and layered structures. Utilizing sort of hydrophilic polymers, for instance polyethylene glycol and polyacrylamide [4] hydrogels can be prepared as optically transparent and fluorescent-free.

In this thesis study, acrylamide- N,N'-bisacrylamide based hydrogels were synthesized via photopolymerization technique using fluorescence active photoinitiators and sensing performance of formed gels were investigated against heavy metal ions and nitroaromatic compounds by using fluorescence spectroscopy. For the purpose of achieving this goal, one-pot photoinitiated synthesis method was utilized owing to its advantages over other functionalization methods such as simple reaction condition, high efficiency and single reaction for both synthesis of hydrogel and functionalization of hydrogel.

2. THEORETICAL PART

2.1. Hydrogels

Although hydrogels have many different definitions, the most popular one is that “Hydrogels are cross-linked, three dimensional polymeric networks with high water absorption capacity.”. Crosslinked polymers insoluble in solvents, but they can absorb solvents. While the water absorption capacities of hydrogels stem from hydrophilicity of the polymeric backbone, insolubility of hydrogels stem from cross-links between polymer chains of gel network (Figure 2.1.).

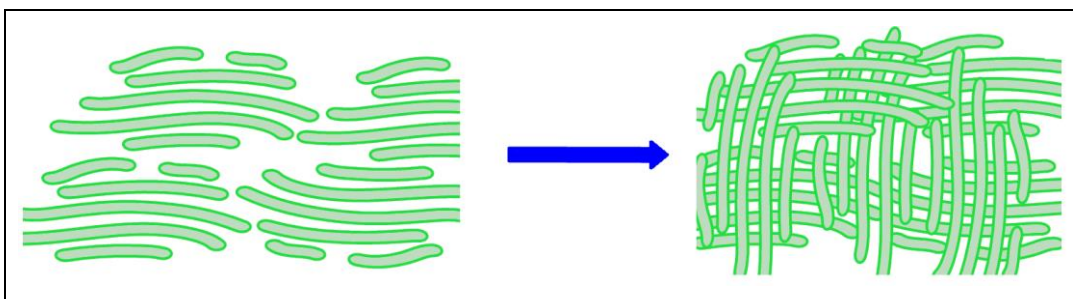


Figure 2.1: Cross-linking in polymer.

2.1.1. Preparation of Hydrogels

According to cross-link type, hydrogels can be divided into two classes as chemically formed hydrogels and physically formed hydrogels. While chemically formed cross-links contain primary bonds, physically formed cross-links contain secondary bonds and chain entanglements.

The most convenient method for preparation of covalently cross-linked hydrogel is chain growth polymerization of monofunctional and multifunctional monomers (Figure 2.2.).

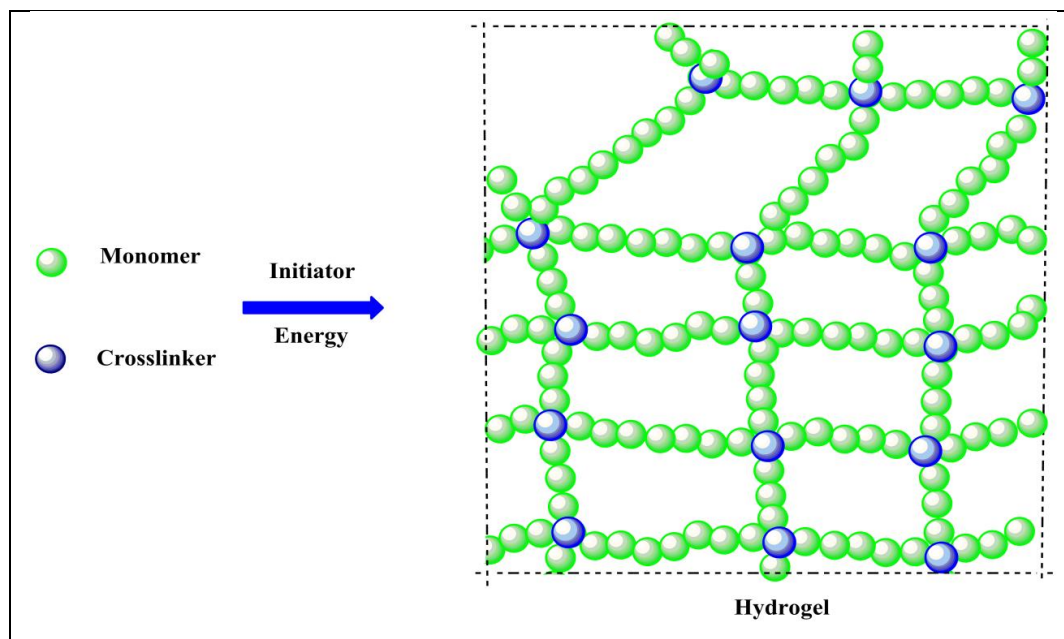


Figure 2.2: Schematic diagram of hydrogel preparation.

Generally free-radical polymerization technique is used for preparation of this hydrogels. Free-radical polymerization contains initiation, propagation and termination steps. Initiation step commonly is achieved via thermal decomposition, redox and photolysis reactions. Once radicalic center formed, radicals transferred from radicalic species to monomers to produce active chains in propagation step. In termination step, due to run out of the monomers polymerization terminates via different mechanism.

2.1.2. Applications of Hydrogels

Owing to their “smart” phase-transition in response to chemical or physical changes, hydrogels have gained special interest in sensing applications. Providing simple, portable and sensitive detection without requirement of instrument or power source, these sensors are directly working devices. Hydrogel sensors are designed by characterizing the analyte stimulated change in physical properties of color and light absorbance, light emission, resonance frequency, light diffraction and refraction.

For instance, adaptation of hydrogels into three-dimensional microarrays for DNA hybridization and protein detection enables highly enhancing the sensor location concentrations [5]. Incorporation of pH-sensitive dye molecules into

hydrogel has presented lifetime sensing procures trustworthy results in light scattering medium [6].

For instance, different sensing forms have been materialized in oxygen detection. Accordingly, for execution in cell culture fermenters an external fiber optic probes were needed to be unified [7]. The mentioned probe based on the oxygen stimulated fluorescence emission quenching of dichlorotris(1,10-phenanthroline)ruthenium(II) hydrate. This fluorescent moiety was immobilized in a photopolymerized poly(ethylene glycol) diacrylate hydrogel. The sensor presented improved repeatability across a series of oxygen concentrations specific for cell culture experiments.

Implantable glucose sensors were fabricated by utilizing the hydrogels as the supporting materials for detection of glucose levels in the body [8, 9]. Responce mechanism of sensors based on interaction between glucose and fluorophore moiety.

Thanks to recent advancements in real time tracing and serveilling of gel attitude (e.g., decomposition, distortion and movement) utilizing optical pulses, fluorescence-emitting moieties containing hydrogel networks have gained great interest. For instance, numerous fluorescence-emitting hydrogel networks have been improved for insulin sensing [10], glucose-sensing [11, 12], temperature sensors [13], control of heavy metal contamination of food and beverages, as well as for monitoring the degradation of hydrogels inside and outside of a living organism [14, 15].

Hydrogels with fluorescent properties, generated by consolidating fluorophore moieties with hydrogel network, have potential uses in probes, bio imaging, tissue engineering and bio assays due to their capable of being injected, fluorescence activities and reliabilities [16] .

First generation heavy metal ion sensors were based on fluorescence quenching affect, since heavy metal ions are strong fluorescence quanchers. Recent improvements have offered 'turn on' sensors with an rice of intensity on heavy metal binding. This sensors were improved for Cu [17] and Hg [18] in water. The nanosensors were constructed with increased detection sensitivity by using metal nanoparticles and quantum dots.

A variety of organic dye molecules, combining anion/cation identifition with fluorescence reporting, have been developed to increase detection sensitivity. Especially certain organic dyes have detection sensitivity in nano-molar level or

sensitivity pretty satisfying for discriminating nontoxic and toxic levels of contaminants [19]. Fluorescent sensors based on genetically engineered living yeast cells for heavy metal ion detection have also been improved.

A smart “turn-off” hydrogel sensor based on 6,7-dihydroxycoumarin fluorophore was synthesized by Whitaker et. al. [20] for organophosphorus nerve agent simulant sensing. Synthesized polyacrylamide hydrogel sensor probe has displayed a remarkable and quiet rapid fluorescence sensing response to the sarin analogous diethylchlorophosphate in the water and air.

Consequently, the utilization of facile synthetic routes for the preparation of hydrogel networks with desired fluorescence characteristics for definite application range is very critical.

The porosity, pore size, pore shape and pore-size distribution of hydrogels can be adjusted by changing reaction composition and conditions.

Fluorescence-emitting moieties containing hydrogel networks, which are covalently bonded with fluorophore molecules, have been commonly utilized in fluorescence monitoring owing to the pliability associative with the selection of fluorophore moieties [21]. Compared with this hydrogels, the synthesis of fluorescence emitting hydrogels via physical blending of fluorophore molecules within a porous hydrogel matrix is a basic and effective procedure [22-24], but it might be restricted by the inhomogeneous distribution of fluorophore moieties [25]. Small molecular and ionic species are diffused into the hydrogels owing to porous structure of hydrogel matrix. Chromophore compounds having bigger dimensions than the pore size can be immobilized in the hydrogel matrix without chemical linkages [26, 27].

In situ synthesis of fluorescent hydrogel sensors, make possible to produce a homogenous dispersion of fluorophore moieties in gel network [28]. However, most of conventional fluorophores (such as fluorescein, rhodamine B) are usually excited in visible-light range, and presents low tissue permeation. A fluorescence-emitting hydrogel sensor with optimum excitation-emission wavelengths, can be fabricated utilizing simple synthesis methods, is extremely aspired.

2.1.3. Sensors

Sensors are devices that have the ability to detect, measure or respond to events such as light, temperature, pressure, ion concentration changes in the physical environment.

Nowadays, sensors have been found wide range of application such as biological analysis, fire alarm systems, prevention of the environmental pollution, monitoring of the manufacturing process and defence sector. A convincing sensor has to present some properties such as occupy minimum space, low-cost, and reliable (sensitive, selective, reproducible) measurement results. Porous structure and large specific surfaces provides enhanced sensitivity and rapid response times to sensor materials.

Amongst the different type of sensors, chemical sensors, which can determine the availability and detect the amount of a specific analyte, has gained special attention. A chemical sensor is a cost effective, mobile, simple and robust tool which sense with excellent and sharp discrimination to a specific analytes available in preferred environment to generate a quantifiable output signal at detectable amount of sample.

Among the chemical sensors, fluorescent sensing is one of the most potent chemical signal transduction mechanisms to report the analyte identification event. Signal transduction is a measurable form of energy, which is produced by which a sensor interacts with its analyte. Most of fluorescent spectroscopy techniques, which lean on the fluorescence emission life time, fluorescence emission anisotropy or fluorescence emission intensity, are extremely sensitive techniques that enable even the recognition of a single molecule. Due to having superb sensitivity, fast analyte response time and nondestructive detection properties, fluorescent chemosensors have advantage against another chemosensors. Moreover, fluorescent sensors is quite practical because of a number of parameters can be adjusted to optimize the fluorescent signal. Basically, change in the intensity of fluorescence signal presents the most direct detectable response to analyte identification.

2.1.4. Fluorescent Sensors for Heavy Metal and Nitroaromatic Compounds

General definition of metal is, materials which are a good conductor of electric and heat. Metals are shiny, hard substances in room temperature, and readily loses their electrons to form positive ions. One of the subclass of metals is heavy metals. Heavy metals are chemical elements which have heavy atomic numbers and densities. Despite this metals are naturally forming species which are found in the earth's crust, they causes detrimental effects on human health or adverse environmental effects. Especially long-term exposure to metals such as mercury, cobalt, lead, nickel, and zinc can cause deleterious health effects in humans [29]. Thus, there is a need for sensor materials which can selectively sense low concentrations of heavy metals (down to nanomoles) in water, since even in such concentrations, these cations may cumulate and exhibit a unfavorable impact.

Nowadays, detection of explosives and hazardous chemicals are being extensively important due to security and health reasons. There is a need for precise, trusted, real time biosensing and chemosensing in the spotlight with the fight against terrorism. Organic molecules which includes at least one nitro group substituted aromatic ring, defined as nitroaromatic compounds. U.S. Environmental Protection Agency has registered these species as environmentally hazardous materials [30, 31]. Amongst them, nitrotoluene and nitrophenols, are substantial contaminants. Trinitrotoluene is well known as an explosive material used in terrorist attacks and mining industry [32-34]. This compound may induce deleterious health effects such as anemia, headaches and skin irritation even at low concentrations. The other strong explosive nitroaromatic compound picric acid is very soluble in aqueous media and can contaminate environment easily [35]. Removal of these pollutants from wastewaters is quite troublesome owing to their resistance to microbial decomposition [36, 37]. For these reason, precise, rapid and sensitive determination of nitroaromatic compounds has critical importance.

It was reported in literature that the fluorescence moieties such as binaphthyl, coumarin, dansyl, pyrene interact with some analytes in the solution by increasing or decreasing the fluorescence activities or altering the fluorescence properties. A number of examples of these recently studied receptors are reviewed below:

It was reported by Kim and Jung et.al. [38] that anthraquinone based chemosensor (Figure-1.3.a) was responsible for copper (II+) cation induced desulfurization. Addition of copper (II+) cations to the media of fluorophore resulted with rapid color change together with its blue-shifted absorption band at ambient conditions, on the contrary, in fluorescence titration study, upon addition of copper (II+) cations to the media of fluorophore resulted with an emission band shift from 590 to 555 nm.

1,8-naphthalimide based selective ratiometric fluorescent sensor probe (Figure-1.3.b) have been synthesized Wang and Peng et al. [39] which acts as a fluorescent ratiometric sensor probe for the mercury (II+) ions in HEPES buffer, whereas upon the addition of different metal cations to the media of fluorophore in MeOH-H₂O (95:5, v/v, pH = 9.0), only gold (III+) cations induce the change of the emission band of fluorophore from 509 to 473 nm.

Sensitive and selective rhodamine based receptor (Figure-1.3.c) has been synthesized by Das and Ganguly et al. [40] which on addition of chromium(III+) and mercury (II+) cations resulted with a "turn-on" response in the visible region of electronic and fluorescence spectra. This fluorophore binds particularly to chromium(III+) and thus could discriminate chromium(III+) and mercury (II+) cations present as a mix in aqueous media, in the availability of excess KI.

Fluorescein aldehyde (Figure-1.3.d) was utilized by Strongin et al. [41] for detecting cysteine and homocysteine by thiazoline ring formation upon nucleophilic addition of the analytes to the aldehyde function. While other amines and thiols were discriminated by this fluorophore, fluorescence intensity of it declined upon addition of homocysteine in deproteinized human plasma.

A symmetrical dansyl based peptide probe, containing two histidine group (Figure-1.3.e) utilizing a disulfide bridge to detect silver (I+) cations in water by "turn-on" response, was synthesized by Lee et al [42]. Sensing performance of this fluorophore was monitored in HEPES buffer solution (pH 7.4). By addition of silver (I+) cations to media, fluorescence emission at the wavelength of maximum intensity of fluorophore increased about 10 times with a blue shift from 524 nm to 500 nm.

Highly selective fluorescent sensor bearing binaphthyl group (Figure-1.3.f) was reported by Wang et al. [43] for the reaction-based relay detection of fluoride and cyanide anions. This sensor showed emission at 480 nm corresponding to intermolecular excimer formation of the 1,1'-binaphthyl fluorophore. Addition of

fluoride anions to the solution of sensor result with the change in emission band (480 nm) and formation of a new peak at 550 nm.

Pyrene functional oligomer (Figure 2.3) was prepared by Yi and Schmuck et al. [44], and utilized as a molecular peptide sensor to detect double stranded-DNA. When sensor molecules bind to nucleic acids, it underwent a conformational alteration from a pleated to a spreaded form that switched the fluorescence of sensor molecules from an excimer emission to a monomer emission.

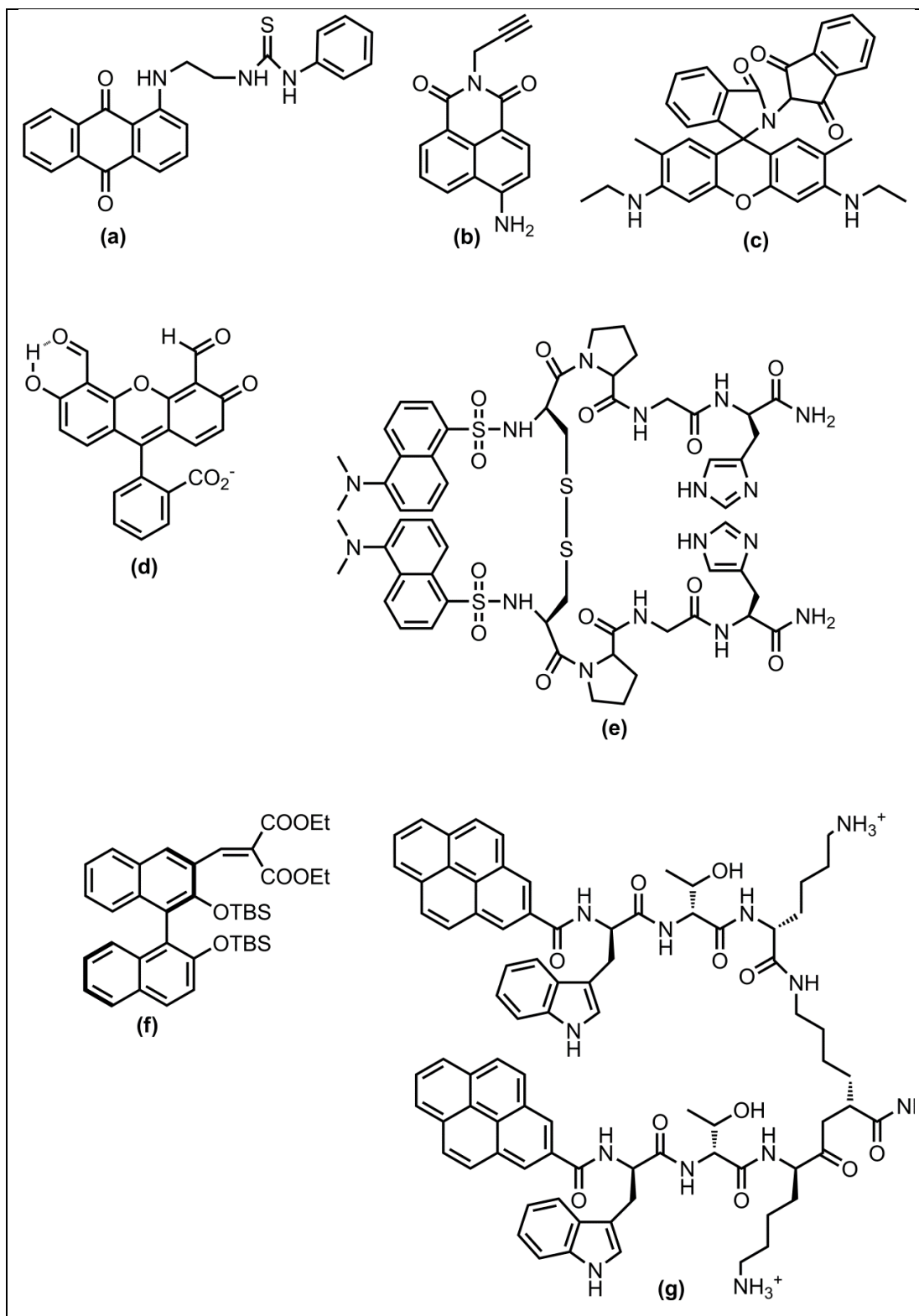


Figure 2.3: Illustration of fluorescence moieties interacting with analytes in the solution.

2.2. Photopolymerization

Due to having powerful and economically affordable synthetic routes, and besides, environment-friendly process in contrast to conventional thermal polymerization reactions, photo-polymerization process is getting more and more popular in polymer industry. The utilization of photolysis process, instead of thermolysis process, to initiate the polymerization reactions cause to a range of advantages, such as solventless process, low-energy consumption, high reaction-rate at ambient conditions and utilization of wide range of monomers.

For material fabrication, photopolymerization is one of the most preferred polymerization technique and utilized over a wide range of applications. Polymerization reactions induced by light, especially in the ultraviolet or visible region of the electromagnetic spectrum, are photopolymerization reactions. These reactions can be initiated by limited molecules which have capability of light absorption in specific wavenumber. After absorption of light by initiator, active center is generated and get involves a kind of reactions such as degradation, hydrogen abstraction, or charge transfer. If needed, the effective wavelength for initiation could be shifted by incorporating minuscule amounts another molecule, named as a photosensitizer, into the system. Absorption of light by photosensitizer results with formation of excited state molecules which are interact with the photoinitiator to generate active species have ability of initiating the polymerization. After the formation of active centers, such as cations and radicals, reactions propagate and terminate similarly as conventional polymerization reactions.

Photo-initiated polymerisation reactions can be categorized as photo-initiated free radical and cationic polymerizations. Though photo-initiated cationic polymerization is getting more and more important in last a few decades, the free radical polymerization is still utilized commonly in such applications due to its applicability to a wide scale of reaction systems established upon vinyl monomers, unsaturated polyesters, and polyurethanes and the presence of photo-initiators.

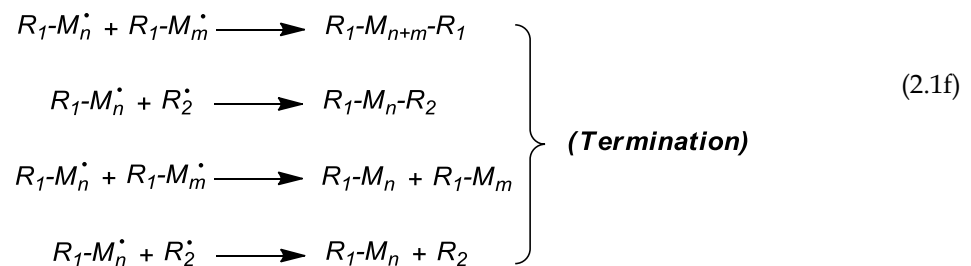
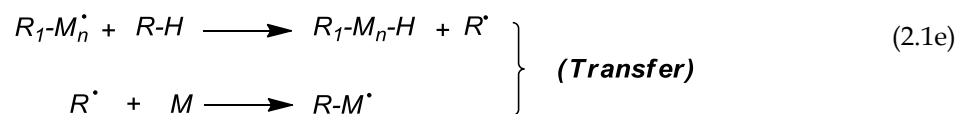
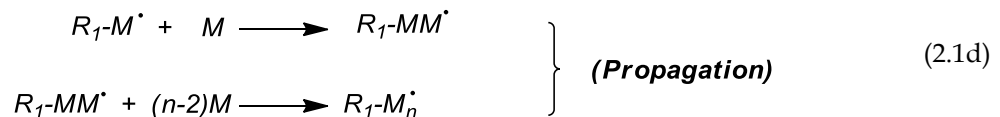
2.2.1. Photoinitiated Free Radical Polymerization

The photopolymerisation take place through photo-initiation (reactions 2.1a-c), propagation, chain transfer, and termination reactions (reactions 2.1d-f).

The mission of the light in photopolymerisation reaction is limited to initial stage, including the absorption and production of active species. The remained steps of photopolymerisation reaction are only thermal processes.



Photo-initiation includes absorption of light by a photosensitizer or energy transfer from a photosensitizer to the light sensitive molecule. Homolytic breaking of a covalent bond results with the formation of a radicalic species which then attacks to a monomer unit. The propagation step includes the addition of chain radical to a carbon–carbon double bond, producing a new radicalic center at the end of the polymer backbone. Propagation step also contains reinitiation of radicals formed by chain transfer reactions.



Eventually, active centers are consumed by bimolecular reaction between active radical chains. Termination step can also form by coupling or disproportion reactions with any other radicalic species.

2.2.1.1. Absorption of Light

Photochemistry is related with interaction of light with material. Once light (optical radiation) absorbed by material, it is converted to energy which induces chemical reactions. The radiation is mostly in the UV or Visible spectral region but is sometimes in the IR spectral region.

Light photons absorbed by any molecule induce electronic excitation. The energy of a photon (E) is given by equation 2.2;

$$E = hc/\lambda \quad (2.2)$$

where h is Planck's constant, c is the velocity of light, and λ is the wavelength. The absorbance A at wavelength λ is given by equation 2.3;

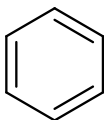
$$A = \epsilon Cl \quad (2.3)$$

where ϵ is constant, C is the concentration of component, and l is the light distance into the medium.

The constant ϵ is called molar absorptivity or extinction coefficient and is a measure of the probability of the electronic transition of a compound at a specific wavelength. The value of molar absorptivity related with the molecule's chemical moiety responsible for the absorption of light, which is named as a chromophore.

Characteristic chromophores include molecular moieties likely to absorb light in the UV-Visible range are π -electron functions and hetero atoms with non-bonding electron pairs [45-47]. A list of certain simple chromophores, their maximum absorption wavelengths, and the molar absorptivity values are given Table 2.1 [45, 46]. Since chromophore group's absorption is directly related with adjacent substituent, given values in Table 2.1 are qualitative. For instance, the absorption and molar absorptivity of conjugated dienes influenced by the number of conjugated double bonds, -alkyl and -aryl substituent [46].

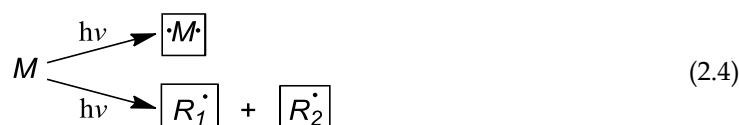
Table 2.1: Molar absorptivity and maximum absorption wavelength of certain chromophore groups.

Chromophore	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$
$\begin{array}{c} \diagup \\ \text{C}=\text{C} \\ \diagdown \end{array}$	195	10,000
$-\text{C}\equiv\text{C}-$	195	2,000
$-\text{N}=\text{N}-$	345	10
NO_2	270	18.6
$\text{S}=\text{O}$	210	1500
$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{C}-\text{OH} \end{array}$	205	60
$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{C}-\text{R} \end{array}$	190 280	900 15
$\begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C}-\text{C}=\text{C} \\ \diagdown \quad \diagup \end{array}$	215	20,000
	185 200 255	60,000 8,000 200

2.2.1.2. Photoinitiation

• Radical Generation by Monomer Irradiation

A few monomers can interact with UV-Visible light and produces radicalic species. There are two suggested ways to photo-initiate polymerization by light-sensitive monomers. As given in reaction 2.4, the biradical generated by a light-induced ring formation or a simple alpha-cleavage of monomer might be liable for initiating photopolymerization.



Formed active monomers can react with normal monomers and lead chain growth. Most commonly used monomers in industry, which undergo polymerisation under UV irradiation are given in Table 2.2 [48, 49].

Table 2.2: Photosensitive monomers.

Allyl methacrylate	Methyl methacrylate
Barium acrylate	1,6-hexanediol diacrylate
Cinnamyl methacrylate	Pentaerythritol tetramethacrylate
Diallyl phthalate	Styrene
Diallyl isophthalate	Tetraethyleneglycol dimethacrylate
Diallyl terephthalate	Tetrafluoroethylene
2-Ethylhexyl acrylate	N-Vinylcarbazole
2-Hydroxyethyl methacrylate	Vinyl cinnamate
2-Hydroxypropyl acrylate	Vinyl 2-furoate
N,N'Methylenebisacrylamide	Vinyl 2-furylacrylate

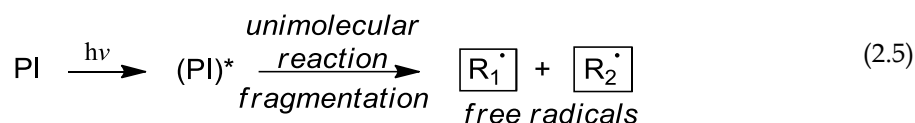
At the same time, due to inadequate absorption properties and low efficiencies under UV irradiation, vinyl monomers, such as styrene, are not used in above mentioned technical applications [45].

• Radicals via Photoinitiators

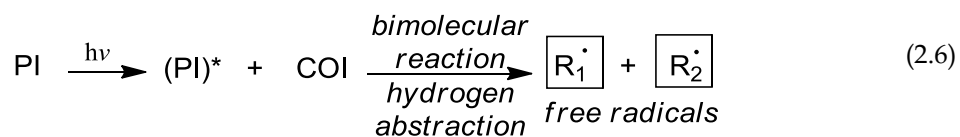
A photoinitiator is a molecule that, under UV or visible light irradiation, undergoes photolytic reaction, producing reactive species. These active species have ability to initiate the polymerisation of convenient monomers.

According to initiating radicals formation process, photoinitiators can be classified into two major categories, designated as Type I and Type II photoinitiators.

“*Type I photoinitiators*”, molecules which undergo unimolecular bond rupture upon absorption of light as given in reaction 2.5.



“*Type II Photoinitiators*”, molecules react with a second molecule to produce radicals in a bimolecular reaction upon absorption of light as given in reaction 2.6.

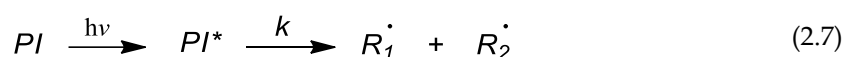


Both *Type I* and *Type II* photoinitiators are effective initiators and widely used in daily life.

Although *Type I* photoinitiators are fairly reactive UV initiators, they are less often utilized in visible light photocuring. Visible light photoinitiators particularly pertain to *Type II* photo-initiators, which are versatile photoinitiators for the UV curing systems.

2.2.1.3. Type I Photo-initiators

Since photoinitiation system includes solely single molecular species, which are regenerate active species, it is named as Unimolecular Photoinitiator Systems. Under UV irradiation, Type I photoinitiators undergo covalent bond rupture and form two radicals. (2.7). Kinetics of a unimolecular reaction is given in (2.8).



$$\frac{d[\dot{R}_1]}{dt} = \frac{d[\dot{R}_2]}{dt} = k [PI^*] \quad (2.8)$$

In a photodecomposition process, when a compound dissociates after absorbing a light quantum, the quantum yield (Φ_R) is the amount of destroyed compounds divided by the amount of photons absorbed by the system. (2.9).

$$\Phi_{R^*} = \frac{\text{Number of initiating radicals formed}}{\text{Number of photons absorbed by the photoinitiator}} \quad (2.9)$$

In theory, type-I photoinitiators should present quantum yield value of two due to two radicals are generated by the photodegradation. Since different deactivation pathway of excited photoinitiator apart from radical formation, monitored quantum yield is quite lower. This pathway contains physical inactivation like fluorescence or non-radiative fading and energy transfer to another un-excited molecules, which is called quenching phase.

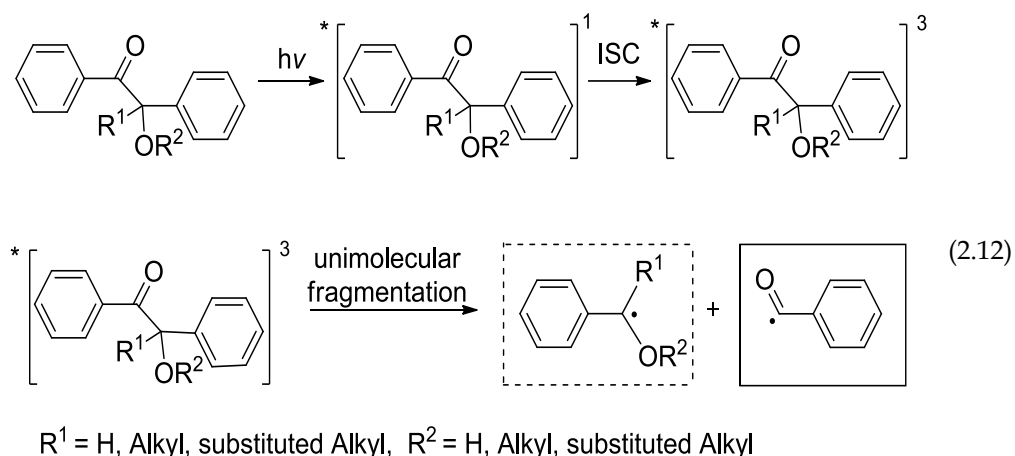
The reactivity of photo generated radicals with monomer species is also to be taken into consideration. Generally, only half of radicals formed initiate the photopolymerization. Remained radicals commonly give coupling or disproportionation reactions. The photoinitiation effectiveness of produced radicals (f_P) can be counted as given below:

$$f_P = \frac{\text{Number of chain radicals formed}}{\text{Number of primary radicals formed}} \quad (2.10)$$

The total photo-initiation effectiveness is stated by the quantum yield of photo initiation (Φ_P) with regard to the given equation:

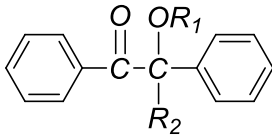
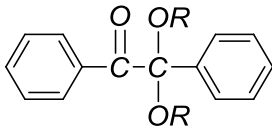
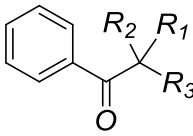
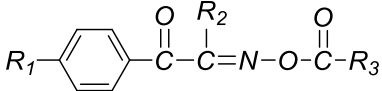
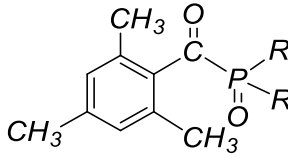
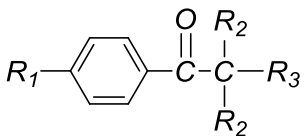
$$\Phi_P = \Phi_{R\cdot} \times f_P \quad (2.11)$$

In respect to needed energy, it should be specified that the energy to excitate the photo-initiator should be higher than the energy to dissociate the bond. Also energy to dissociate the bond should be high enough to provide stability to molecule.



Type-I photo-initiators that undergo a photolytic cleavage under light irradiation and form radicals enable to induce photopolymerization. As given reaction 2.12, when photo-initiator is irradiated by UV-light, it is absorb the ultraviolet light resulting with excited electron state and rapid inter-system crossing to the triplet-state. In this state, the single-bond between benzoyl group and alkyl carbon is broken, generating an carbonyl radical and remained fragment. Though the formed benzoyl radical mainly initiates polymerization, in some instances, the remained radical may involve the initiation. The commonly utilized *Type-I* photoinitiators are given in (Table 2.3) such as acylphosphineoxides, alpha-aminoketones, benzoin derivatives phenones, benzil ketals and hydroxylalkyl [50-53].

Table 2.3: Structures of typical *Type I* radical photoinitiators.

Photoinitiators	Structure	$\lambda_{\max}$ (nm)
Benzoin ethers	 $R_1 = H, \text{ alkyl}$ $R_2 = H, \text{ substituted alkyl}$	323
Benzil ketals	 $R = CH_3, C_3H_7, CH_2$	365
Acetophenones	 $R_1 = OCH_3, OC_2H_5$ $R_2 = OCH_3, H$ $R_3 = C_6H_5, OH$	340
Benzyl oximes	 $R_1 = H, SC_6H_5$ $R_2 = CH_3, C_6H_{13}$ $R_3 = C_6H_5, OC_2H_5$	335
Acylphosphine Oxides	 $R = C_6H_5 \text{ or } OCH_3$	380
Aminoalkyl phenones	 $R_1 = SCH_3, \text{ morpholine}$ $R_2 = CH_3, CH_2Ph \text{ or } C_2H_5$ $R_3 = N(CH_3)_3, \text{ morpholine}$	320

2.2.1.4. Type II Photo-initiators

Type-II photo-initiators are also known as bi-molecular photo-initiators due to two type of molecules are required to generate the active radical: a light absorbing photo-initiator and a hydrogen or electron donor molecule which is named as co-

initiator. These photo-initiators do not give Type-I reactions since the irradiation energy to excite this molecules inadequate for bond cleavage. Nevertheless, the excited molecule has ability to react with hydrogen or electron donor molecule to produce radicals to initiate polymerization as given in reaction 2.13. In this situation, reaction presents bi-molecular reaction kinetics (2nd order) (2.14).



$$\frac{d[R_1^\bullet]}{dt} = \frac{d[R_2^\bullet]}{dt} = k [PI^*] [COI] \quad (2.14)$$

In Type-II initiation process, light absorption occurs in the near ultraviolet and visible ranges. Radicalic species are produced via hydrogen excision or photoinduced electron transfer mechanisms above mentioned.

• Hydrogen abstraction

Photo-initiators which carry on with a hydrogen abstraction process can be illustrated by association of benzoyl-benzene and a hydrogen donor as given in reaction 2.15. As hydrogen donor (R-H) is an amine including transferable hydrogen, benzoyl-benzene transfer an electron to donor molecule by abstracting a hydrogen to generate an active radical and semi-pinacol radical. The semi-pinacol radical is not effective enough to induce polymerization and generally undergo reaction with terminating species resulting a decrease in the polymerisation velocity.

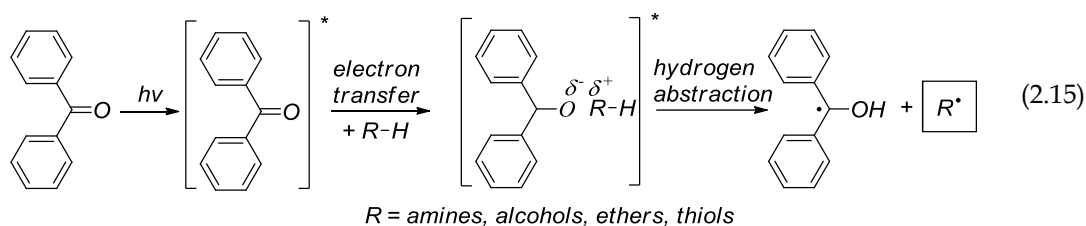
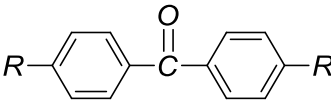
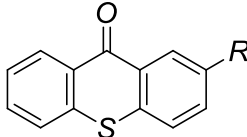
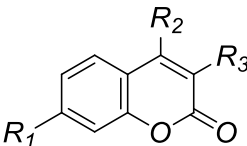
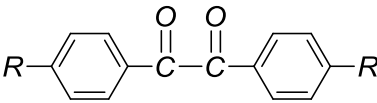
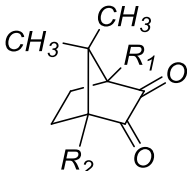


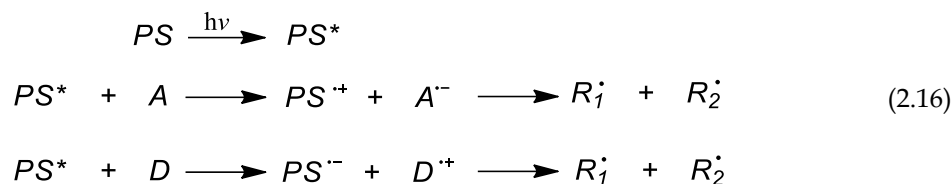
Photo-sensitizers of Type-II initiation system including benzo phenones, camphorquinones, thioxanones, benzyl and ketocoumarin derivatives are given in Table 2.4.

Table 2.4: Structures of typical *Type II* photosensitizers.

Photosensitizers	Structure	$\lambda_{\max}$ (nm)
Benzophenones	 $R = H, OH, N(C_2H_5)_2, C_6H_5$	335
Thioxanthenes	 $R = H, Cl, isopropyl$	390
Coumarins	 $R_1 = N(C_2H_5)_2,$ $N(CH_3)_2$ $R_2 = CH_3,$ <i>cyclopentane</i> $R_3 = benzothiazole, H$	370
Benzils	 $R = H, CH_3$	340
Camphorquinones	 $R_1 = CH_3, H$ $R_2 = H, CH_3$	470

- Photo-induced electron transfer (PET) and succeeding decomposition

Photo-PET is a quite broad mechanism that is not restricted with specific molecules and is essential as an initiation reaction including the most of bi-molecular photo-initiating process. The photo-excited molecules (photo-sensitizer) can behave as electron acceptor or donor during the interaction between co-initiator. The radical ions formed after the PET process can generally degrade to initiating radicalic species (2.16).



Electron transfer is frequently monitored for benzylic ketone-amine systems and usually with dye-coinitiator systems. Dye molecules cover big part of visible-light photo-initiators since excited states of dye's are readily obtained. Co-initiator molecules, for instance trialkyl amine, are needed because of dye photo-chemistry involve either a photolytic reduction or photolytic oxidation mechanisms. Wide range of dye-strips exist for choosing of an convenient visible initiation range and are given in Table-2.5 [54-57].

Table 2.5: Absorption Wavelength of Some Dye Molecules.

Dye	Absorption wavelength
Thiazine	Around 675
Acridine	Around 475
Xanthene	500–550
Fluorone	450–550
Coumarin	350–450
Cyanine	400–750
Carbazole	400

Whether the dye molecule oxidized or reduced rely on the coinitiator; for instance, methylthioninium chloride can be reduced photolytically by taking an electron from an tertiaryamine or oxidized photolytically by giving an electron to benzyltrimethylstannane [54]. Both reactions result with the generation of an active radicalic centers which can initiate the polymerization.

2.2.1.5. Monomers

Vinylic monomers, which comprise π -bonds between adjacent C atoms ($C=C$), are widely utilized in free radical photo-polymerization reactions. Radicalic species attacks to monomer by opening the unsaturated carbon-carbon double bond and

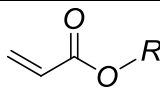
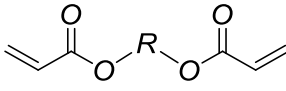
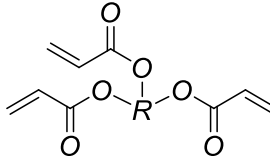
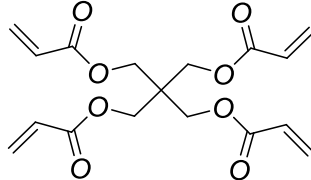
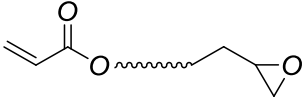
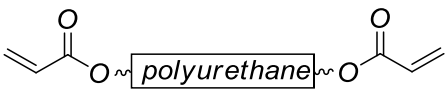
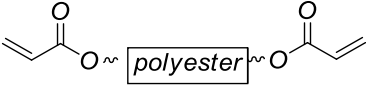
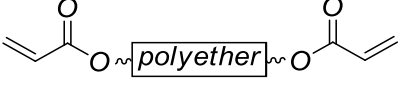
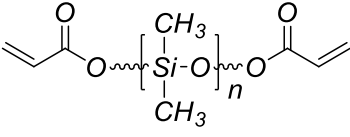
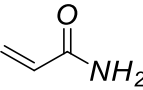
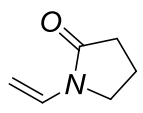
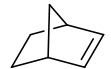
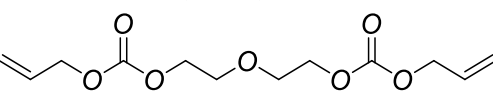
simultaneously regenerating a reactive center. The formed radicalic center thereafter joins to other monomer unit. Numerous monomers with double-bond are enable to give radical polymerization since radicalic species are uncharged and do not entail electron donating or withdrawing groups to conjugate the charge on the active center, just as in anionic or cationic polymerization reactions. Commercial concerns identify monomer reactivity and product properties during the formulation. Since acrylic acid derivatives have very high reaction rates [58], they are largely utilized in free radical photo-polymerization process. The general structures of aforementioned monomer molecules is given in Table 2.6. Having high reaction rates, makes acrylates favorable in film and coating applications which requires fast processing.

While mono-functional acrylates decrease the thickness of the pre-polymer formulation for readily processing, multi-functional acrylates enhance the mechanical properties of formed polymer, such as durability to organic solvers and impact resistance via cross-linked sturcture [58, 59].

The main handicap of (meth)acrylate monomers is their volume shrinkage, due to displacement of long distance secondary (Van der Waals) bonds with short distance primary (covalent) bonds between monomer units. The volume shrinkage leads serious problems including a large build-up of internal stress, which causes fault formation and volume alterations, which can decrease mechanical properties. A favorable way to decrease the shrinkage of volume is to utilize polimerizable acrylate oligomers.

Diallyl diglycolcarbonate has been utilized for along times in optic materials such as production of contact-lense [60]. Acryl amide is utilezed in stereolithography and to produce prototypes [62-63]. N-vinyl pyrrolidinone is co-polymerized with (meth)acrylates for beauty product and bio-medical applications [64]. Norbornylene is polymerized with thiol compounds for fiber optic coating compositions [65].

Table 2.6: Chemical structures of free radical polymerizable monomers.

Monomers	Structure
Methyl acrylate, Ethyl acrylate, Butylacrylate, 2-Hydroxyethyl acrylate, 2- Ethylhexyl acrylate	 $R = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_2\text{H}_4\text{OH}, \text{C}_4\text{H}_9$
1,4-Butanediol diacrylate, Neopentyl glycol diacrylate, 1,6-Hexanediol diacrylate, 1,10-Decamethylene diol diacrylate, Diethylene glycol diacrylate, Dipropylene glycol diacrylate, Tetraethylene glycol diacrylate Tripropylene glycol diacrylate	 $R = \text{C}_4\text{H}_8, \text{C}_5\text{H}_{10}, \text{C}_6\text{H}_{12}, \text{C}_{10}\text{H}_{20},$ $\text{C}_4\text{H}_8\text{O}, \text{C}_6\text{H}_{12}\text{O}, \text{C}_8\text{H}_{16}\text{O}_3, \text{C}_9\text{H}_{18}\text{O}_2$
Glycerol triacrylate Trimethylolethane triacrylate Trimethylolpropane triacrylate Pentaerythritol triacrylate	 $R = \text{C}_3\text{H}_5, \text{C}_5\text{H}_9, \text{C}_6\text{H}_{11}, \text{C}_5\text{H}_9\text{O}$
Pentaerythritol tetraacrylate	
Epoxy acrylates	
Urethane acrylates	
Polyester acrylates	
Polyether acrylates	
Silicone acrylates	
Acryl amide	
N-vinylpyrrolidinone	
Norbornene	
Diallyldiglycolcarbonate	

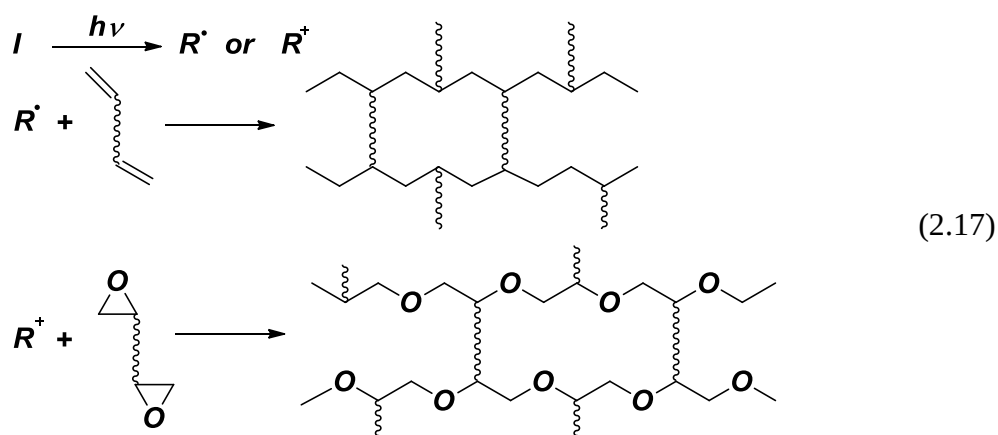
2.2.2. Photocrosslinking

The area of photo-crosslinking of monomeric, oligomeric, and polymeric species are attracting increasingly more attention in polymer technology.

Many commercial applications, such as coating, ink, adhesive, photo-imaging and photolithography, optical lense, wire insulating materials, are based on photo-crosslinked polymers. Photo-curing and photo-polymers has became of subject of many scientific research and literature review [45, 50, 59, 66-82]. The photo-crosslinking of polymers can be described as the procedure which light is utilized to induce the cross-linking of preformed polymers with functional groups. More precisely, under light radiation macromonomers having more than two functional groups per macromonomer starts cross-linking to a three-dimensional polymer network. Corss-linked three-dimensional polymer networks can also be obtained cross-linking agents having more than one functional groups.

2.2.2.1. Photocrosslinkers

Bi- and poly-functional monomer molecules serves as crosslinkers. Alkylene glycol acrylates, trimethylol propane and penta erythritol, triallylcyanurate, and triallyl- isocyanurate are largely utilized crosslinkers (2.17).



3. RESEARCH OBJECTIVES

Hydrogels are unique material class, which are composed of a self supporting, water swollen three-dimensional elastic network, and enable diffusion of analyte molecules and enhanced surface area for binding target analytes. Due to their matchless morphology, hydrogels provides an ideal supporting matrix for further functionalization towards a wide range of applications.

In this thesis study, we have intended to synthesize of functional porous structured hydrogels with specific properties (e.g. fluorescence active) to expand their applications. For the purpose of achieving this goal, one-pot photoinitiated synthesis method was utilized owing to its advantages over other functionalization methods such as simple reaction condition, high efficiency and single reaction for both synthesis of hydrogel and functionalization of hydrogel.

Firstly, dansyl functional acrylamide based hydrogel (DNS-Gel) was synthesized by utilizing dansyl fluorophore as photoinitiator without any functionalization, in photopolymerization of acrylamide as monomer and N,N'-methylenebisacrylamide as crosslinker (Figure 3.1). This method involves the irradiation of dansyl chloride which results with generation of free radicals inducing the polymerization of monomeric species.

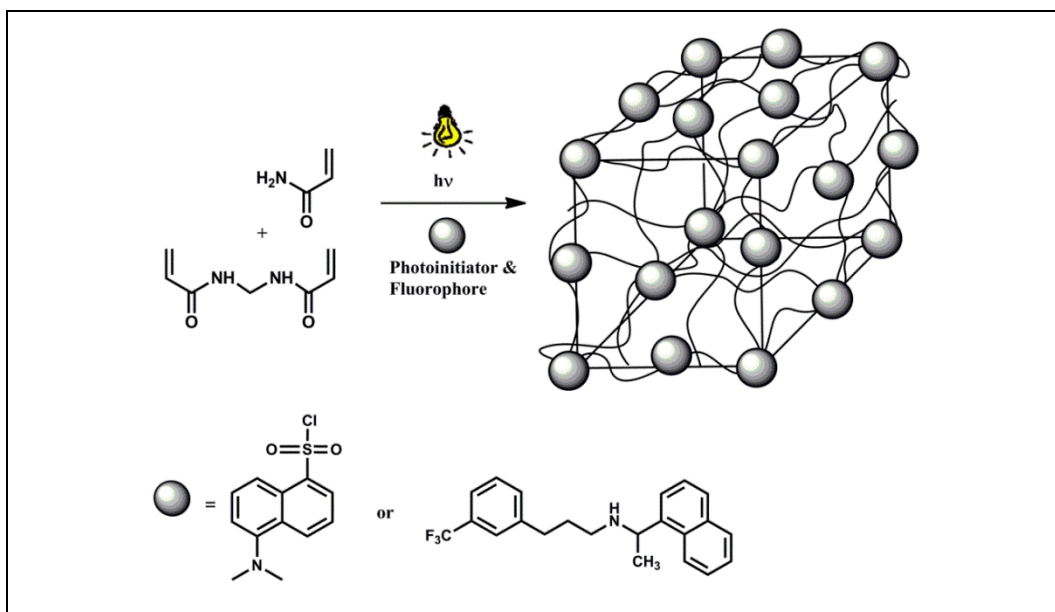


Figure 3.1: Synthesis of dansyl/cinacalcet functional polyacrylamide hydrogels by free radical photopolymerization.

There were three different functional groups, namely, dimethylamino, naphthalene and sulfonyl chloride in the chemical structure of the dansyl chloride. Among them, the naphthalene moiety was well-known photosensitive group that can absorb both visible and UV radiations and as a fluorophore owing to its sensitivity and efficiency and excimer emission in the visible-range of electromagnetic spectrum.

It has been observed that in the presence of cobalt, mercury and lead ions, fluorescent activity of dansyl moieties in hydrogel network significantly decreased and increased again when washed with ACN:Water (1:1). It is also observed that in the presence of nitroaromatic compounds picric acid (PA) and 2, 4-dinitrophenol (2,4-DNP) fluorescent activity of dansyl moieties in hydrogel network significantly decreased and increased again when washed with ACN:Water (1:1). This phenomena makes possible to utilize DNS-Gel as selective heavy metal ion and nitroaromatic compound sensor in water media (Figure 3.2). Comparatively cost effective, simple preparation, and possibility of direct use in aqueous media differentiate our sensor material from others.

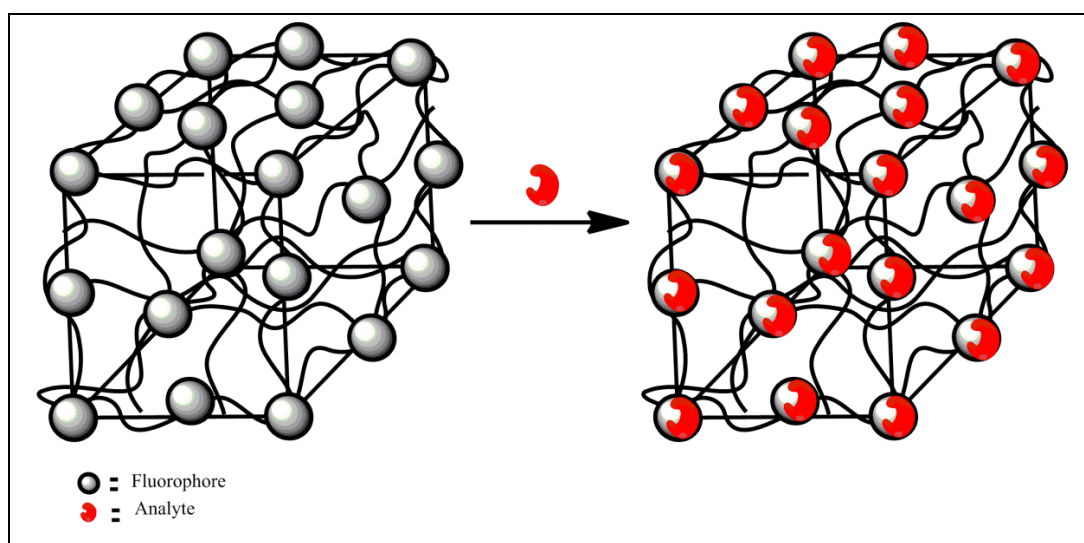


Figure 3.2: Illustration of sensing of analytes by dansyl/cinacalcet functional polyacrylamide hydrogels.

Secondly, cinacalcet functional acrylamide based hydrogel (CIN-Gel) was synthesized by utilizing cinacalcet fluorophore as photoinitiator without any functionalization, in photopolymerization of acrylamide as monomer and N,N'-methylenebisacrylamide as crosslinker (Figure 3.1). This method also involves the

irradiation of cinacalcet hydrochloride which results with generation of free radicals inducing the polymerization of monomeric species. There were three different functional groups, namely, naphthalene, secondary amine and trifluoro-toluene in the chemical structure of the cinacalcet chloride. Among them, the naphthalene moiety was well-known photosensitive group that can absorb both visible and UV radiations and as a fluorophore owing to its sensitivity and efficiency and excimer emission in the visible-range of electromagnetic spectrum.

It has been observed that in the presence of zinc ions, fluorescent activity of cinacalcet moieties in hydrogel network significantly decreased and increased again when washed with ACN:Water (1:1). It is also observed that in the presence of nitroaromatic compound trinitrotoluene (TNT) fluorescent activity of cinacalcet moieties in hydrogel network significantly decreased and increased again when washed with ACN:Water (1:1). This phenomena makes possible to utilize CIN-Gel as selective heavy metal ion and nitroaromatic compound sensor in water media (Figure 3.2). Comparatively cost effective, simple preparation and possibility of direct use in aqueous media differentiate our sensor material from others.

4. MATERIAL AND METHOD

4.1. Materials

The chemicals and their properties used in this study are listed in Table 4.1.

Table 4.1: The chemicals used in synthesis, purification and measurement processes.

Chemical	Supplier	Cas No	Assay
Acetonitrile	MerckMillipore	75-05-8	≥ 99.9%
Acrylamide (AAm)	Alfa Aesar	79-06-1	99.0%
Cadmium chloride	Alfa Aesar	10108-64-2	99.0%
Chloroform	Sigma-Aldrich	67-66-3	≥99.9%
Cinacalcet hydrochloride	Lupin	364782-34-3	≥ 99 %
Cobalt (II) chloride hexahydrate	Alfa Aesar	7791-13-1	98.0%
Dansyl chloride	Alfa Aesar	605-65-2	≥ 97.0 %
Diethylether	Sigma-Aldrich	60-29-7	≥99.9%
Lead(II) acetate trihydrate	Merck	6080-56-4	99.0%
Manganese(II) chloride dihydrate	Merck	20603-88-7	≥ 99.0%
Mercury(II) chloride	Alfa Aesar	7487-94-7	≥ 98.0%
Methanol	Sigma-Aldrich	67-56-1	99.8%
Methylene chloride	Sigma-Aldrich	119-61-9	99%
Nickel(II) chloride	Aldrich	7718-54-9	98.0%
N,N'-methylenebisacrylamide(BAAm)	AppliChem	110-26-9	99.0%
Tin(II) chloride	Sigma-Aldrich	7772-99-8	≥99.99%
Zinc acetate	Aldrich	557-34-6	99.99%
1,2-dinitrobenzene (1,2-DNB)	Sigma-Aldrich	528-29-0	≥99%
2,4-dinitrophenol (2,4-DNP)	Sigma-Aldrich	51-28-5	≥98%
2,4-dinitrotoluene (2,4-DNT)	Sigma-Aldrich	121-14-2	97%
2,4,6-trinitrophenol (picric acid, PA)	Sigma-Aldrich	88-89-1	≥98%
2,4,6-trinitrotoluene (TNT)	Sigma-Aldrich	118-96-7	1 mg/mL in
4-nitrophenol (4-NP)	Sigma-Aldrich	100-02-7	≥99%
4-nitrotoluene (4-NT)	Sigma-Aldrich	99-99-0	99%

4.2. Equipment

4.2.1. Photoreactor

A Kerman type photoreactor equipped with 12 Philips 8W / O6 lamps emitting light nominally at 350 nm was used.

4.2.2. Electron spin resonance spectrometer (ESR)

The X-band Electron spin resonance (ESR) spectra were recorded using a Bruker EMX EPR spectrometer. Solution of dansyl chloride and cinacalcet hydrochloride in different solvents (chloroform, acetonitrile, diethylether and acetonitrile-water mixture) were irradiated upon UV-light for 2 hours in NMR tubes and then the samples were placed in a resonance chamber in a magnetic field.

4.2.3. UV-visible Spectrophotometer

UV-Vis spectroscopy measurements of the samples were recorded at room temperature on a Shimadzu UV-2101 spectrophotometer. Quartz cuvettes (1 cm path length) were used for UV-Vis spectra.

4.2.4. Fluorescence Spectrophotometer

Flourecence spectroscopy measurements of the samples were recorded at room temperature on a Varian Eclipse spectrofluoremeter. Quartz cuvettes (1 cm path length) were used for fluorescence spectra.

For the flourecence spectroscopy measurements of gel samples, a piece of gel (rectangular form with 15 mm length, 7 mm wideness and 1.2 mm thickness) was immobilized in a cuvette with 10 mm path length for quenching experiments. Various solutions with different amount of quencher concentrations were injected into this cuvette and waited for a minute before taking fluorescent spectra. The

samples were excited at 350 nm wavelength for DNS-Gel and at 250 nm wavelength for CIN-Gel.

3.2.5. Scanning electron microscope

The morphology of the gel samples were analysed by Thermo Scientific-Quanta 200 FEG model scanning electron microscope. For Scanning electron microscopy (SEM) analysis, thin sample sections of freeze dried gel samples were placed on double-sided adhesive tape and mounted on a specimen.

4.3. Sample Synthesis

4.3.1. Synthesis of Linear PMMA Polymer

MMA (20 mmol) was dissolved in anisole (1.20 mL) in a single-necked flask under oxygen-free argon atmosphere. Ethyl 2-bromoisobutyrate (EBIB) (0.20 mmol) as initiator then was added to a polymerisation flask, followed by PMDETA (0.40 mmol), copper (I) bromide (0.2 mmol), respectively. The reaction mixture was degassed with a slow stream of argon for 20 min. and placed in a water bath at 90 °C to initiate polymerization. At this point, the mixture was stirred for 12 h. The solvent was then evaporated, and the residue was dissolved in a minimum amount of DCM. The formed polymer was precipitated in methanol. For further purification, polymer was dissolved in DCM, and then precipitated in excess amount of methanol. Then, it was filtered using (G4) glass filter and dried.

4.3.2. Synthesis of Linear DNS-PMMA Polymer

Linear dansyl-poly(methyl-methacrylate) (PMMA) polymer was prepared through free radical photopolymerization of methyl-methacrylate (20 mmol) monomer by using dansyl chloride (0.02 mmol) as photoinitiator in 1 ml chloroform. For this purpose, nitrogen-flushed and sealed samples were prepared in quartz reaction tube and were photocured at room temperature for 4 hours in a photoreactor

in which the samples were surrounded by a circle of 12 lamps emitting light nominally at 350 nm.

4.3.3. Synthesis of Linear CIN-PMMA Polymer

Linear cinacalcet-poly(methyl-methacrylate) (CIN-PMMA) polymer was prepared through free radical photopolymerization of methyl-methacrylate (20 mmol) monomer by using cinacalcet hydrochloride (0.02 mmol) as photoinitiator in 2 ml chloroform. For this purpose, nitrogen-flushed and sealed samples were prepared in quartz reaction tube and were photocured at room temperature for 4 hours in a photoreactor in which the samples were surrounded by a circle of 12 lamps emitting light nominally at 350 nm.

4.3.4. Synthesis of Dansyl Containing Hydrogel (DNS-Gel)

The dansyl containing hydrogels were prepared through free radical photopolymerization of AAm/BAAm (7 mmol/ 0.09 mmol) by using dansyl chloride (0.022 mmol) as photoinitiator in 1.5 g of solvent mixture (1:1 Acetonitrile/Distilled water mixture (w/w)). For this purpose, nitrogen-flushed samples were prepared and injected between two glass slides separated by a 1.5 mm thick silicone gasket and were photocured at room temperature for 4 hours in a photoreactor in which the samples were surrounded by a circle of 12 lamps emitting light nominally at 350 nm. The light intensity at the location of the samples was measured by a Delta Ohm model HD- 9021 radiometer (10.0mW/cm²). After synthesis of dansyl containing AAm/BAAm hydrogel (DNS-gel), the gels were transferred into solvent mixture (1:1 Acetonitrile/ Deionized water (w/w)) immediately. Finally, each sample was stored in an excess of solution at room temperature for at least 24h to keep them at their equilibrium state and to remove unreacted monomer and initiator molecules from the gels. The yield was determined gravimetrically after the hydrogels were washed and dried (yield >92%).

4.3.5. Synthesis of Cinacalcet Containing Hydrogel (CIN-Gel)

The cinacalcet containing hydrogels were synthesized via free radical photopolymerization of AAm:BAAm (7 mmol: 0.09 mmol) by using cinacalcet chloride (0.04 mmol, 0.08 mmol and 0.16 mmol) as photoinitiator in 1.5 g of solvent mixture (1:1 Acetonitrile/Distilled water mixture (w/w)). For this purpose, nitrogen-flushed samples were prepared and injected between two glass slides separated by a 1.5 mm thick silicone gasket and were photocured at room temperature for 4 hours in a photoreactor in which the samples were surrounded by a circle of 12 lamps emitting light nominally at 350 nm. The light intensity at the location of the samples was measured by a Delta Ohm model HD- 9021 radiometer (10.0 mW/cm²). After synthesis of cinacalcet containing AAm/BAAm hydrogel (CIN-gel), the gels were transferred into solvent mixture (1:1 Acetonitrile/ Deionized water (w/w)) immediately. Finally, each sample was stored in an excess of solution at room temperature for at least 24 h to keep them at their equilibrium state and to remove unreacted monomer and initiator molecules from the gels. The yield was determined gravimetrically after the hydrogels were washed and dried. (yield >96%).

4.4. Characterization and Performance Evaluation of Samples

4.4.1. Swelling measurements

The swelling experiments were conducted gravimetrically by utilizing samples wiped with pre-moistened filter paper to remove excess water after incubation of samples in distilled water for 24 h.

Swelling ratio (SR) was calculated using following mathematical expressions:

$$SR = (W_s - W_d) / W_d \quad (4.1)$$

W_s and W_d represent weight of equilibrium swollen gel and weight of dry gel, respectively.

4.4.2. Fluorescence Sensing Measurements of DNS-Gel Against Heavy Metal Cations and Nitroaromatic Compounds

A definite amount of DNS-gel was placed in quartz cell containing solvent mixture to provide the amount of DNS group to be 4.1×10^{-6} mol. Then, DNS-gel was treated with prescribed amount of heavy metal cations (Cd^{2+} , Co^{2+} , Hg^{2+} , Pb^{2+} , Mn^{2+} , Ni^{2+} , and Zn^{2+}) and nitroaromatic compounds (TNT, 2,4-DNT, 2,6-DNT, 2-NT, 3-NT, PA, 2,4-DNP, 4-NP, and 1,2-DNB). The fluorescent responses of DNS-gel were measured by fluorescence spectroscopy at room temperature.

4.4.3. Fluorescence Sensing Application of CIN-Gel Against Heavy Metal Cations and Nitroaromatic Compounds

A definite amount of CIN -gel was placed in quartz cell containing solvent mixture to provide the amount of CIN group to be 1.25×10^{-5} mol. Then, CIN-gel was treated with prescribed amount of heavy metal cations (Pb^{2+} , Sn^{2+} and Zn^{2+}) and nitroaromatic compounds (4-NT, 4-NP, 1,2-DNB, 2,4-DNT, 2,4-DNP, PA and TNT). The fluorescent responses of CIN-gel were measured by fluorescence spectroscopy at room temperature.

Fluorescence properties of CIN-gel in different solvents also has been studied by performing measurements in ACN, water, ACN: water mixtures with different ratios w/w (3 : 1), (1 : 1) and (1 : 3) respectively.

5. RESULTS AND DISCUSSION

5.1. DNS Studies

5.1.1. Initiation Mechanism of DNS

Arenesulfonyl halides can be used not only as an initiator, but also as chain transfer agent in radical polymerization [83]. In recent years, arenesulfonyl halides have been shown to be efficient initiators for metal-catalyzed atom transfer radical polymerization (ATRP) due to their fast radical generations as well as the low dimerization tendency of formed sulfonyl radicals. As result, well-controlled polymerization of a large number of vinyl monomers including (meth)acrylates, styrenes, acrylonitrile, and vinyl chloride were achieved by using arenesulfonyl halides as initiators in the ATRP process [84]. The sulfonyl chlorides were also utilized as chain-transfer-agent in the free radical polymerization of styrene and methyl methacrylate and large chain transfer constants between 0.007 and 0.015 were found for growing polystyrene chains to sulfonyl chlorides [85].

There were three different functional groups, namely, dimethylamino, naphthalene and sulfonyl chloride in the chemical structure of the dansyl chloride. Among them, the naphthalene moiety was a well-known photosensitive group that can absorb both visible and UV radiations. In our case, two possible radical generating mechanisms of dansyl chloride (DNS) were proposed based on type I and type II photoinitiation systems. In the type I route, the sulfonyl chloride moiety of excited singlet of DNS could undergo homolytic cleavage into naphthylsulfonyl and chloride radicals under UV light irradiation. (Figure 5.1).

Whereas, the excited triplet of DNS abstracted hydrogen from another ground state DNS and generated active aminoalkyl and inactive naphthyl radicals in the type-II route. Overall, the naphthylsulfonyl and aminoalkyl radicals could efficiently initiate the photocrosslinking of acrylamide and *N,N'*-methylene bisacrylamide to form corresponding DNS containing hydrogels (Figure 5.1).

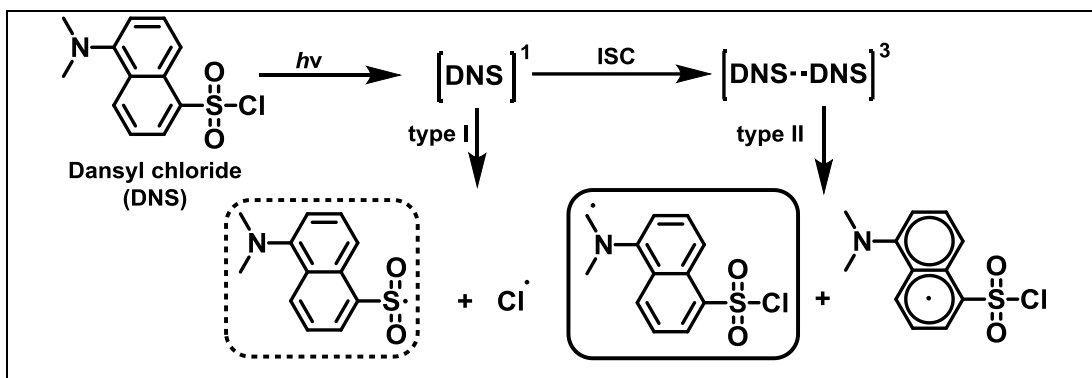


Figure 5.1: Plausible photoinitiation mechanism of dansyl chloride.

In order to gain more insight into the initiation mechanism, the spectral changes of DNS solution (in water/acetonitrile, v:v = 1:1) during UV light irradiation were recorded as a function of irradiation time. According to Figure 5.2, the absorption band of DNS at 260 and 365 nm were significantly decreased, whereas, the new band at 310 nm was appeared. After 150 minutes, the maximum absorption spectrum at 365 nm was reduced to 71% of its initial value. Although this absorption spectrum was decreased gradually, it was still observable throughout the polymerization period. As a result, it was concluded that the DNS was photochemically decomposed and participated in the initiation of the photocrosslinking process.

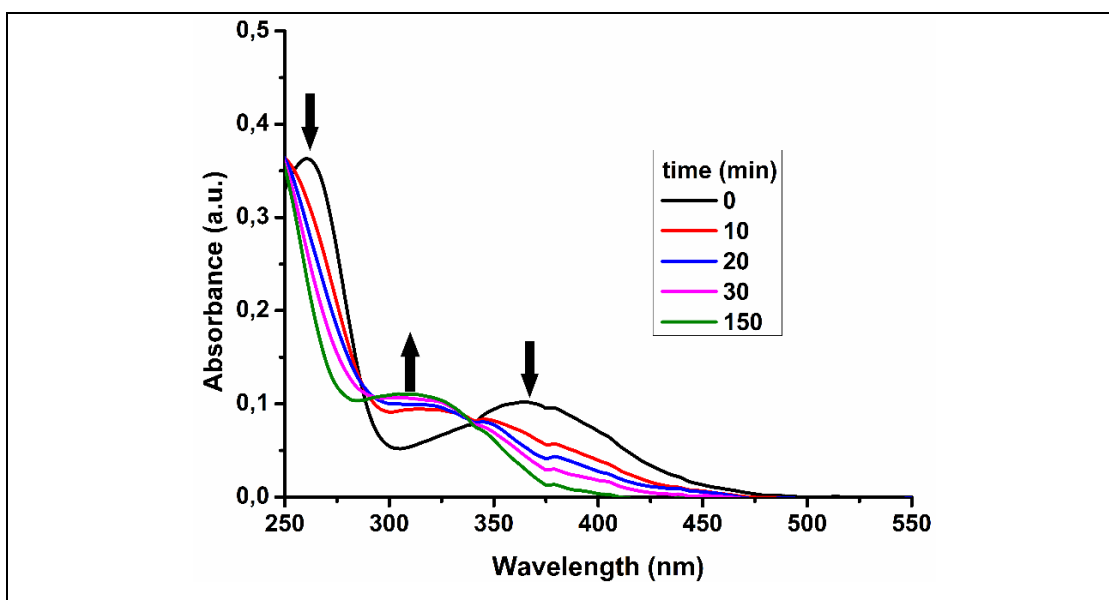


Figure 5.2: Photobleaching behavior of the photoinitiating system in a formulation consisting of dansyl chloride (1.2×10^{-5} M) in water/acetonitrile, (w:w = 1:1) during irradiation at 350 nm (light intensity = 10.0 mW/cm^2) in a quartz cell with 0.5 mm thickness at room temperature.

The photoinitiation mechanism of DNS was also investigated via electron paramagnetic resonance (EPR) spectroscopy at ambient conditions (Figure 5.3). The photochemical radical formation of DNS was investigated in acetonitrile, diethyl ether, chloroform, and acetonitrile-water mixture under UV irradiation. Upon 2h photoradiation, the corresponding radical species was only detected in chloroform solution. This was probably caused by its shorter lifetime in acetonitrile, diethyl ether, and acetonitrile-water solutions compared to the chloroform solution. In the EPR spectrum of DNS, the free radical peak was split to three peaks due to interaction even if it was weak with nucleus spin of the nitrogen atom. It can be regarded as a sign that both the free radical peak is formed and that it interacts with nitrogen on the structure.

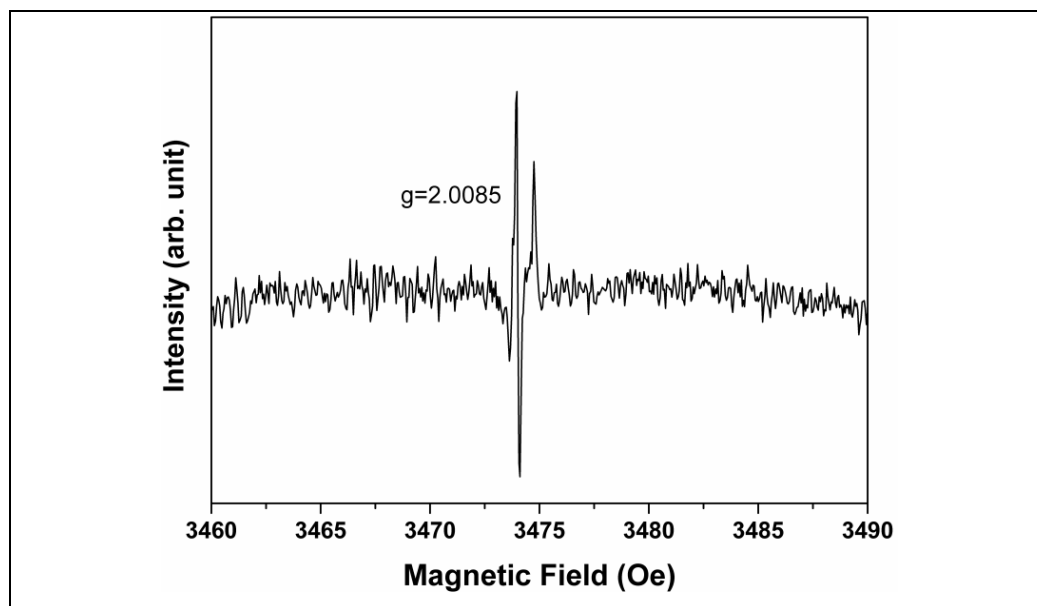


Figure 5.3: EPR spectrum of DNS in chloroform after UV-light irradiation for 2 h at room temperature.

Additionally, the availability of DNS moieties in the hydrogel was verified by a model study. The synthesis of linear poly(methyl-methacrylate) using DNS as a photoinitiator was accomplished under similar experimental conditions. By comparing UV spectra of linear DNS-PMMA with PMMA, the characteristic DNS band between 245 and 285 nm was clearly observed in Figure 5.4.

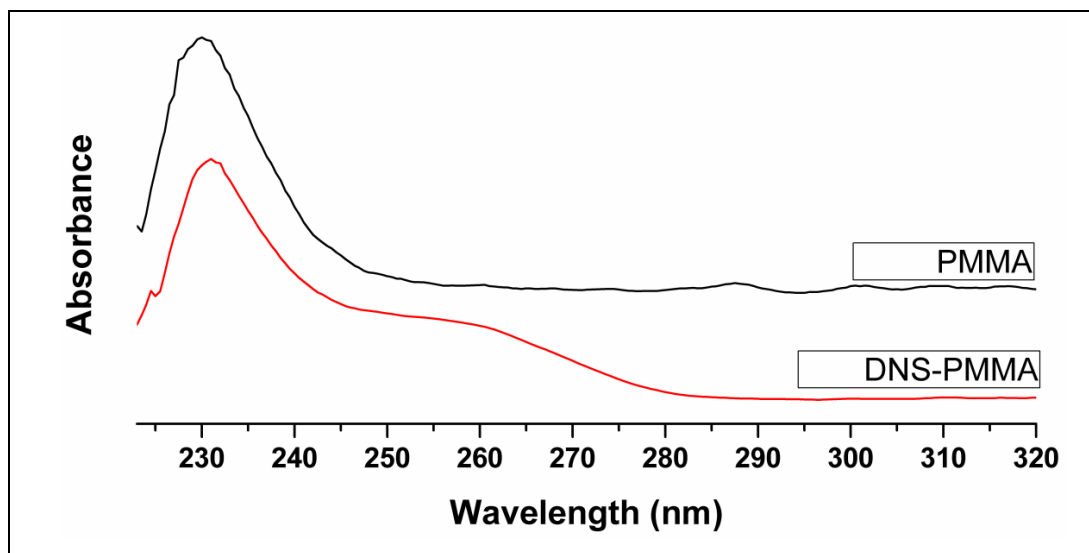


Figure 5.4: Comparison of UV-spectra of linear-PMMA and linear-DNS-PMMA and (2.0×10^{-5} M in methylene chloride).

5.1.2. Preparation of DNS-gel

In the light of mechanistic studies, the DNS-functionalized hydrogels were prepared through photopolymerization of acrylamide/*N,N'*-methylenebisacrylamide in water/acetonitrile under UV irradiation for 4 hours (average conversion >92%) (Figure 5.5).

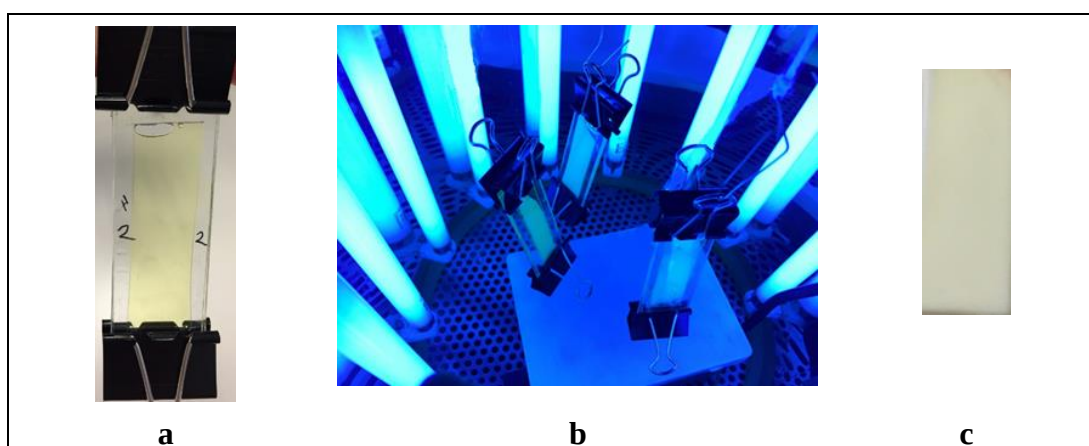


Figure 5.5: Images of DNS-Gel Before a), Upon b) and After c) irradiation.

Scanning electron microscopy was used to determine the morphology of freeze-dried DNS-gel samples. SEM images of dansyl containing gels were presented in Figure 5.6. As shown in SEM images, the DNS-gels displayed a

macroporous structure along its whole volume with interconnected pores in the size range 10-30 μm . DNS-gel matrix has swelling ratio of 6.3.

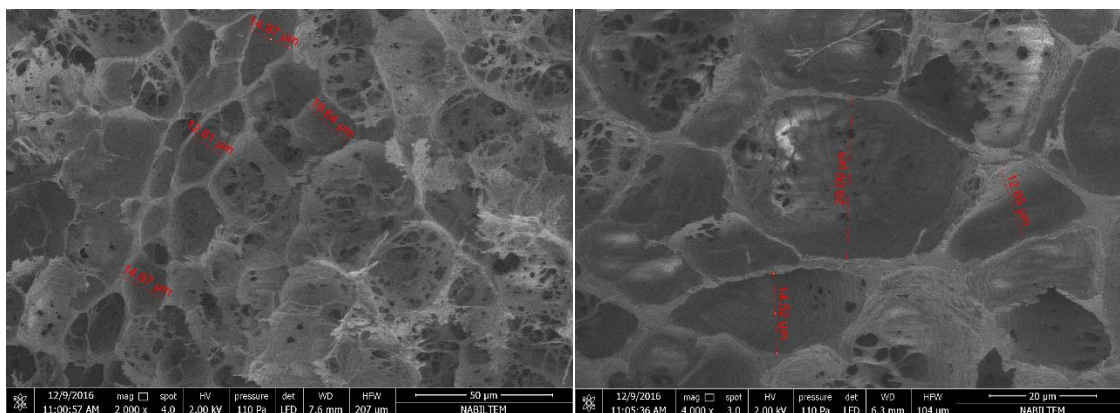


Figure 5.6: SEM images of the dansyl functional hydrogels.

5.1.3. Sensing Applications of DNS-Gel

The binding and recognition behavior of the dansyl functional acrylamide hydrogel (DNS-gel) towards different metal cations and nitroaromatic compounds were investigated via fluorescence measurements. Metal cations and nitroaromatic compounds sensing experiments were conducted in ACN:water (1:1) solvent system at 350 nm excitation wavelength at room temperature. Dansyl fluorophore of DNS-gel gave a very strong emission spectrum in the absence of any metal cations due to intramolecular charge transfer (ICT) from nitrogen atom of the dimethylamino group to naphthalene moiety in the related fluorescence emission spectra for metal cations (Figure 5.7 and Figure 5.8) and nitroaromatic compounds (Figure 5.9 and Figure 5.10) [37, 52]. When DNS-gel was titrated with 100 equivalents of metal cations (Cd^{2+} , Co^{2+} , Hg^{2+} , Pb^{2+} , Mn^{2+} , Ni^{2+} , and Zn^{2+}), ICT emission of DNS-gel was quenched remarkably with slight red-shifting of the band maxima. The quenching of the emission intensity of DNS-gel was attributed to electron transfer from the excited DNS to nearby metal cations. As seen from Figure 5.7, the interferences resulting from other cations are not significant. Quenching mechanism of dansyl group by metal cations due to complexation between N and O atoms of pending amid groups in the polymer chain and sulphonyl group of dansyl moiety. Masoud et al. were reported that the all complexes between the polycrylamide ligand and metals have

octahedral geometric structure containing the metal ions which have strong affinity for coordinated to both N- and O- donor ligands via resonance [86, 87].

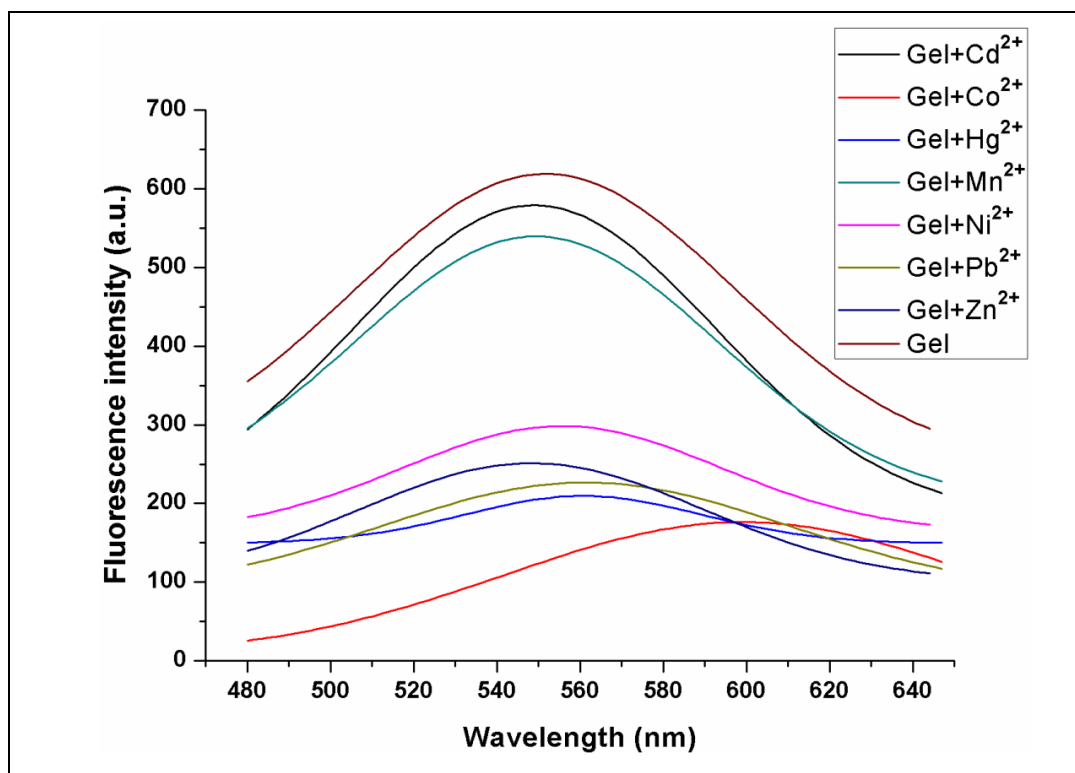


Figure 5.7: Fluorescence spectral responses of **DNS-gel** (containing 4.1×10^{-6} mol DNS) in ACN:water (1 : 1, v/v) upon addition of 100 eq. of Cd^{2+} , Co^{2+} , Hg^{2+} , Pb^{2+} , Ni^{2+} , Mn^{2+} , and Zn^{2+} cations.

Among the studied metal cations, the highest quenching efficiency was observed for Co^{2+} . The evolution of fluorescence emission spectra of DNS-gel upon titration with Co^{2+} cation at different equivalent (Eq.) ratios is depicted in Figure 4.8. The fluorescence intensity was found to decrease significantly as a function of concentration. Besides, dansyl fluorophore of DNS-gel gave very linear responses to the addition of Co^{2+} cation up to 50 eq with R^2 value of 0.99 (Figure 5.8). These results indicate that DNS-gel could be employed as Co^{2+} sensing fluorescence chemical probe.

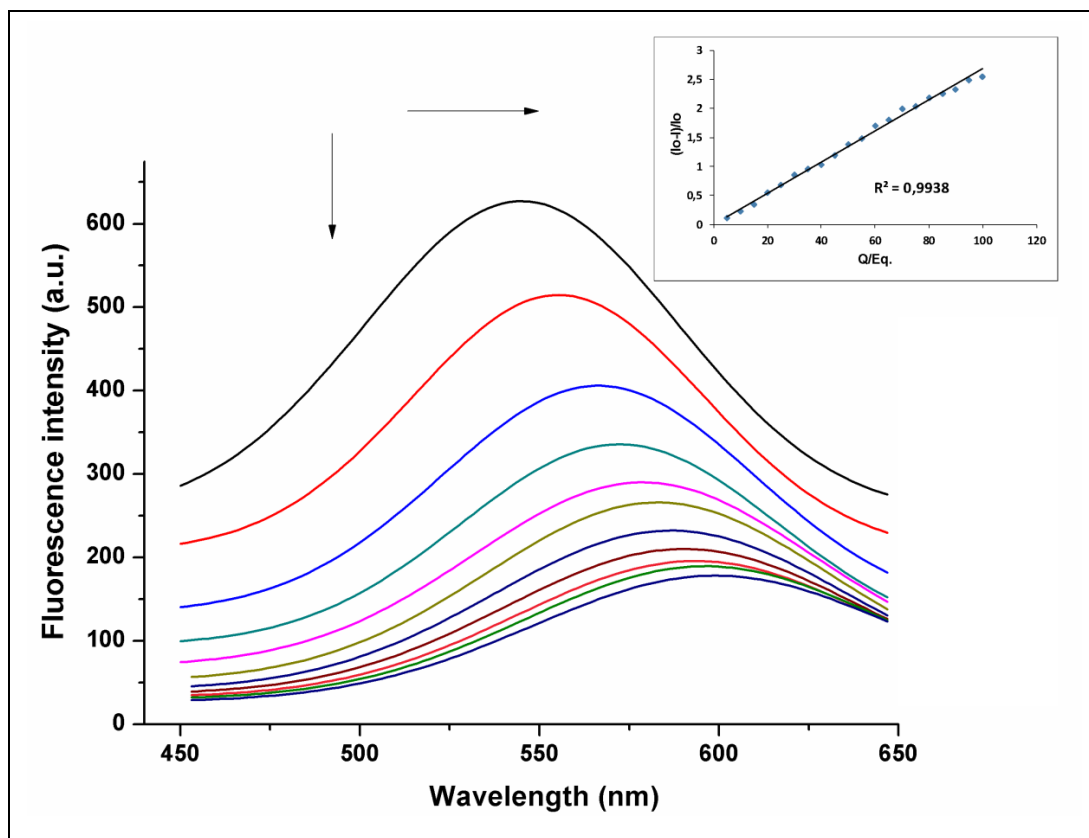


Figure 5.8: Fluorescence emission spectra of DNS-gel (containing $4.1 \cdot 10^{-6}$ mol DNS) in ACN :water (1:1) in the presence of Co^{2+} cation at 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 equivalent ratios.

Quenching efficiency ratios (QE) of the metal cations and nitroaromatic compounds were calculated from the equation 5.1:

$$\text{QE} = \frac{(I_0 - I)}{I_0} \times 100 \quad (5.1)$$

The obtained results for metal cations were demonstrated in Figure 5.9. The highest QEs among the studied metal cations were observed for Co^{2+} (72.56%). As shown in Figure 5.9, except for Hg^{2+} and Pb^{2+} , other background metal ions had small interferences for the fluorogenic determination of Co^{2+} cation suggesting that DNS-gel could be employed as a potential Co^{2+} chemical probe.

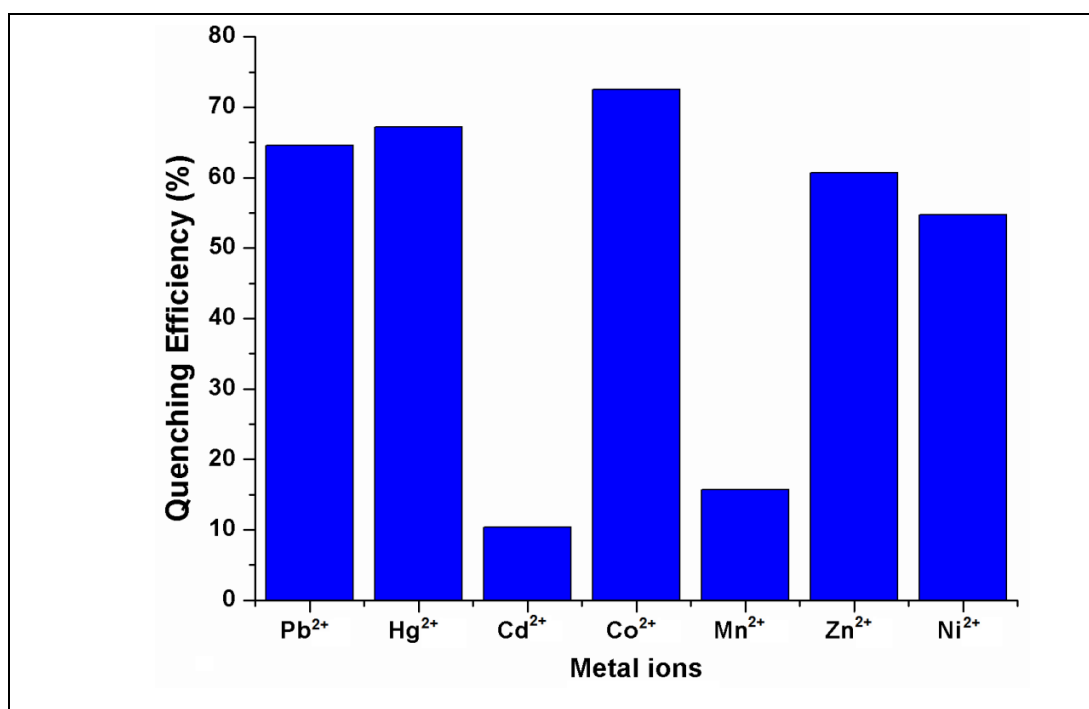


Figure 5.9: QE intensities of the DNS-gel upon adding of 100 eq. aimed heavy metal ions.

The sensing performance was found to be selective toward toxic metal cations, even in the presence of nitroaromatic compounds cations such as 1,2-DNB, 4-NP, 2, 4-DNP, PA, 4-NT, 2, 4-DNT and TNT. The fluorescence emission spectra of DNS-gel upon addition of 0.1 equivalent of nitroaromatic compounds are given in Figure 5.10. It can be seen from the figure that all nitroaromatic compounds in this study quenched fluorescence emission of dansyl fluorophore efficiently. When DNS-gel was titrated with 0.1 eq. of nitroaromatic compounds, ICT emission of DNS-gel was showed slightly blue-shifted quenched emission band. The remarkable quenching and blue shifting of the emission intensity of DNS-gel was ascribed to electron transfer from the DNS fluorophore in the excited to nitroaromatics PA and 2,4-DNP were showed the highest quenching efficiency among all nitroaromatics. The electron transfer from dansyl moiety to nitroaromatic compounds was very likely to responsible from fluorescence quenching. Fang et al. have presented the crucial act in electron transfer in the quenching process of nitroaromatic compounds by comparing the electron deficiency degrees of aromatic compounds during quenching process. Also, they were reported the quenching efficiencies emission of acrylamide had smaller effect than dansyl quencher group [88].

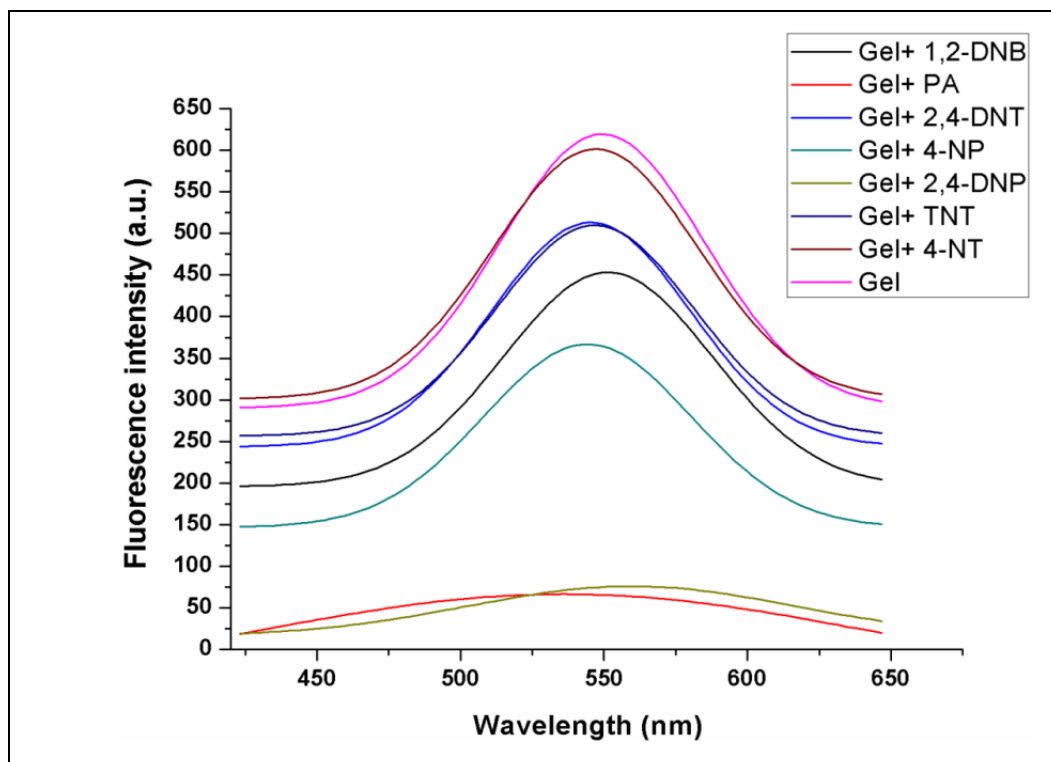


Figure 5.10: Fluorescence spectral response of DNS-gel (containing 4.1×10^{-6} mol DNS) in ACN:water (1 : 1, v/v) upon addition of 0.1 eq. of 1,2-DNB, 4-NP, 2, 4-DNP, PA, 4-NT, 2, 4-DNT and TNT.

Quenching efficiency ratios (QE) of the nitroaromatic compounds were calculated and the obtained results were demonstrated in Figure 5.11. The highest QEs among the studied nitroaromatic compounds were observed for PA (88.55%) and 2,4-DNP (86.50%). It might be understood from Figure 5.11, the interferences caused by remained compounds were negligible.

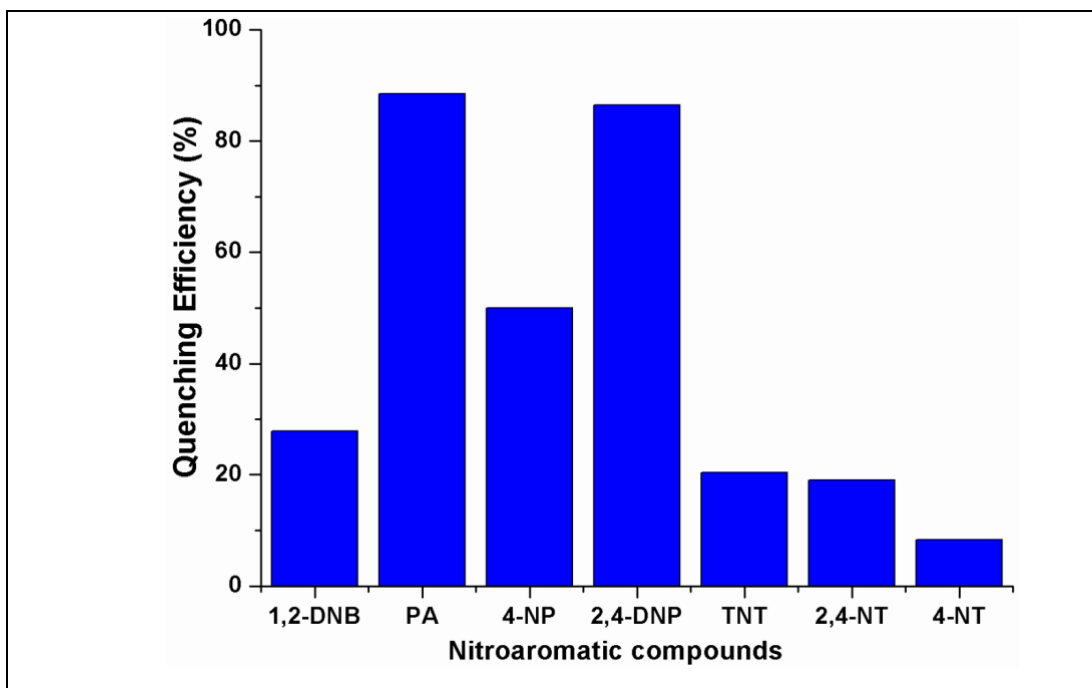


Figure 5.11: QE of the DNS-gel upon addition of 0.1 eq. aimed nitroaromatic compounds.

The evolution of fluorescence emission spectra of DNS-gel upon titration with PA at different equivalent (eq.) ratios is depicted in Figure 5.12. The Stern–Volmer plot in the inset of Figure 5.12 suggests that the quenching process of DNS-gel by the addition of PA is rather linear with the increasing concentration of the quencher. These results indicate a dynamic (collisional) quenching mechanism in which energy of the excited fluorophore was transferred nonradiatively to the quencher [53, 54]. Besides, dansyl fluorophore of DNS-gel gave very linear responses to the addition of PA cation up to 0.1 eq with R^2 value of 0.99 (Figure 5.12).

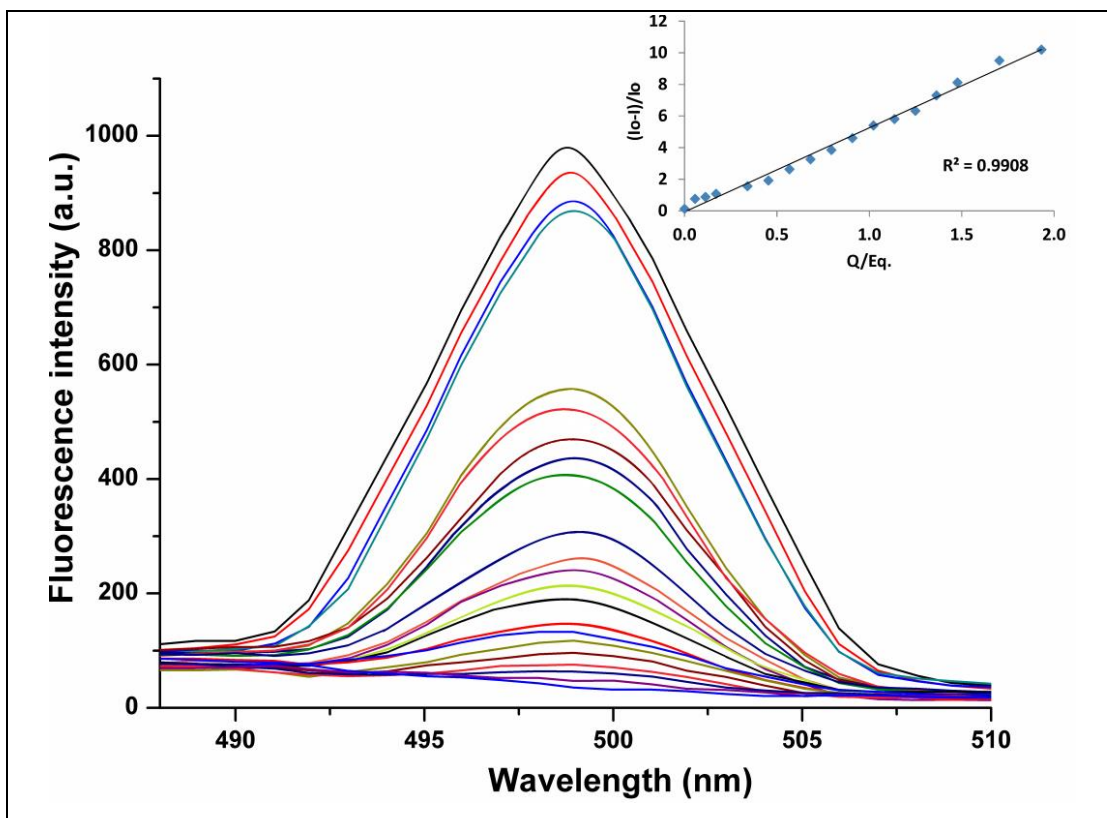


Figure 5.12: Fluorescence emission spectra of DNS-gel (containing 4.1×10^{-6} mol DNS) in ACN :water (1:1) in the presence of PA 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09 and 0.10 eq. ratios.

5.2. CIN Studies

5.2.1. Initiation Mechanism of CIN

The UV–vis spectrum of CIN shows a strong absorption at 295 nm, a shoulder peaks at 282 nm and 305 nm peculiar to naphthalene analogs [89, 90] and a relatively weak absorption signal at 228 nm in ACN/Water, (1:1, w/w) (Figure 5.13). The fluorescence emission spectrum of CIN in ACN/Water is shown in Figure 5.13. The emission spectrum of CIN demonstrates a broad band having a main peak at 335 nm which was attributed to interaction between the naphthalene group and the amino group in ACN/Water (1:1, w/w).

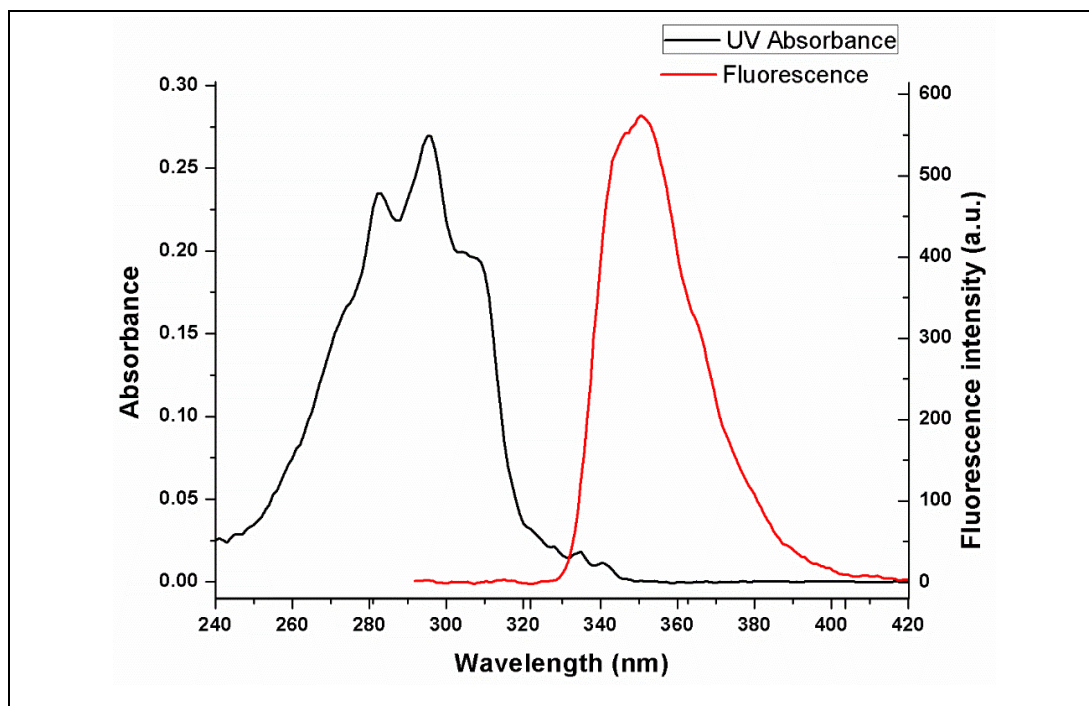


Figure 5.13: UV-Visible (Black) and Fluorescence (Red) spectrums of Cinacalcet HCl (0.06 mg/ml) in ACN/Water (1:1).

In order to gain more insight into the photoinitiation mechanism of cinacalcet, the change in the optical absorption spectrum of the polymerization solution was recorded as a function of irradiation time. As can be seen from Figure 5.14, with increasing irradiation time, the absorption spectra at 283 nm did not changed.

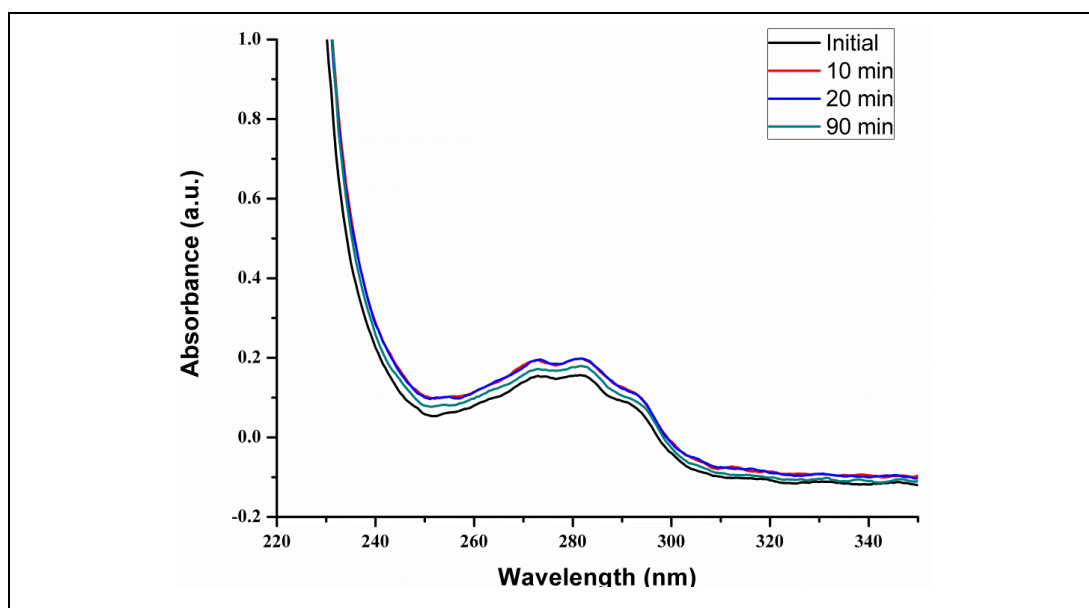


Figure 5.14: UV-spectra of cinacalcet chloride (0.06 mg/ml) in ACN/Water (1:1) after UV-light irradiation.

The presence of CIN groups in the CIN-gel network was further demonstrated by synthesizing linear poly(methyl-methacrylate) (PMMA) by initiated with CIN in methanol. By comparing UV spectra of linear CIN-PMMA with PMMA, the characteristic CIN peak at 227 nm and a broad peak at 245 nm were clearly observed in Figure 5.15.

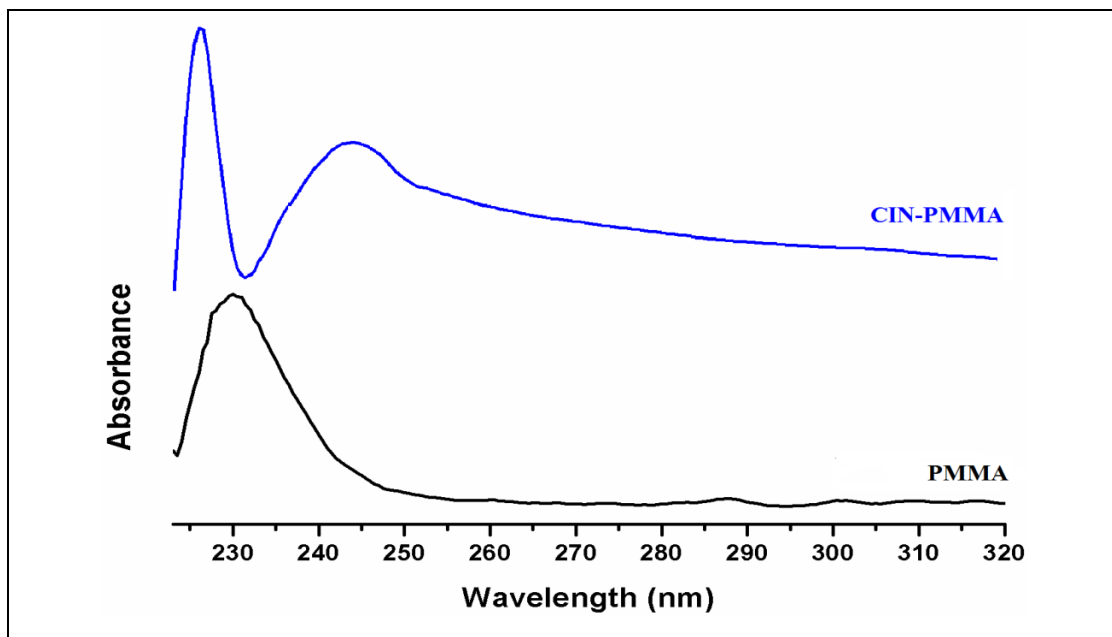


Figure 5.15: Comparison of UV-spectra of linear-PMMA and linear-CIN-PMMA and (2.0×10^{-5} M in methylene chloride).

5.2.2. Synthesis of CIN-Gel

In this study cinacalcet functional gels were prepared via photopolymerization of acrylamide- N,N' -bisacrylamide using cinacalcet hydrochloride as photoinitiator under UV irradiation in one-pot manner. In order to optimize fluorophore concentration of hydrogels, three different gels were synthesized by changing cinacalcet ratio. After the hydrogels were washed and dried, monomer conversions were determined gravimetrically (average conversion >96%).

The morphology of freeze-dried CIN-gel samples was determined by Scanning electron microscopy (SEM). SEM images of CIN- gels were given in Figure 5.16. As can be seen from SEM images, CIN-gel has a macroporous structure along its whole volume with interconnected pores in the size range 8-30 μm . CIN-gel matrix has swelling ratio of 3.5.

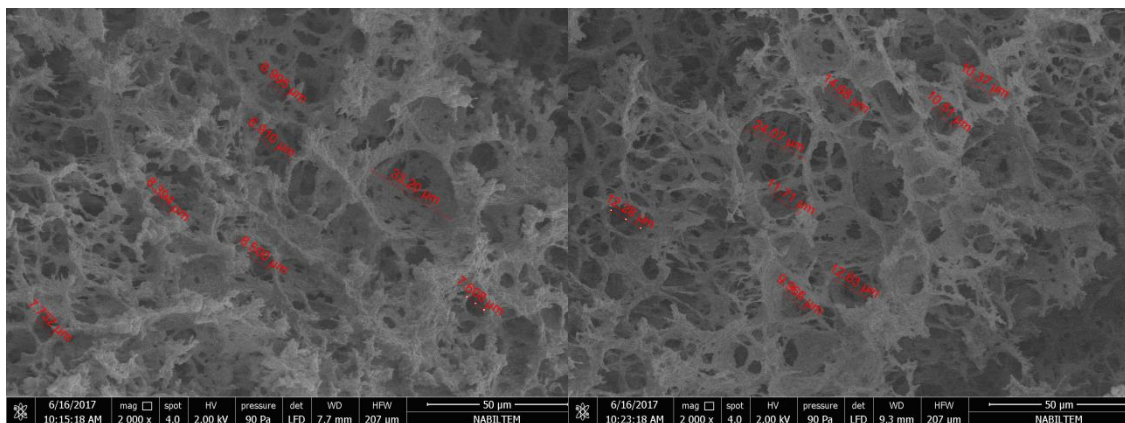


Figure 5.16: SEM images of the cinacalcet functional hydrogels.

5.2.3. Sensing Applications of CIN-Gel

For optimization of cinacalcet amount in hydrogels, of synthesized cinacalcet functional acrylamide hydrogels (CIN-gel) towards nitroaromatic compound 2, 4-DNP were investigated via fluorescence measurements (Figure 5.17). Cinacalcet amount was chosen as 8×10^{-5} mol due to efficiency and feasibility of reaction conditions.

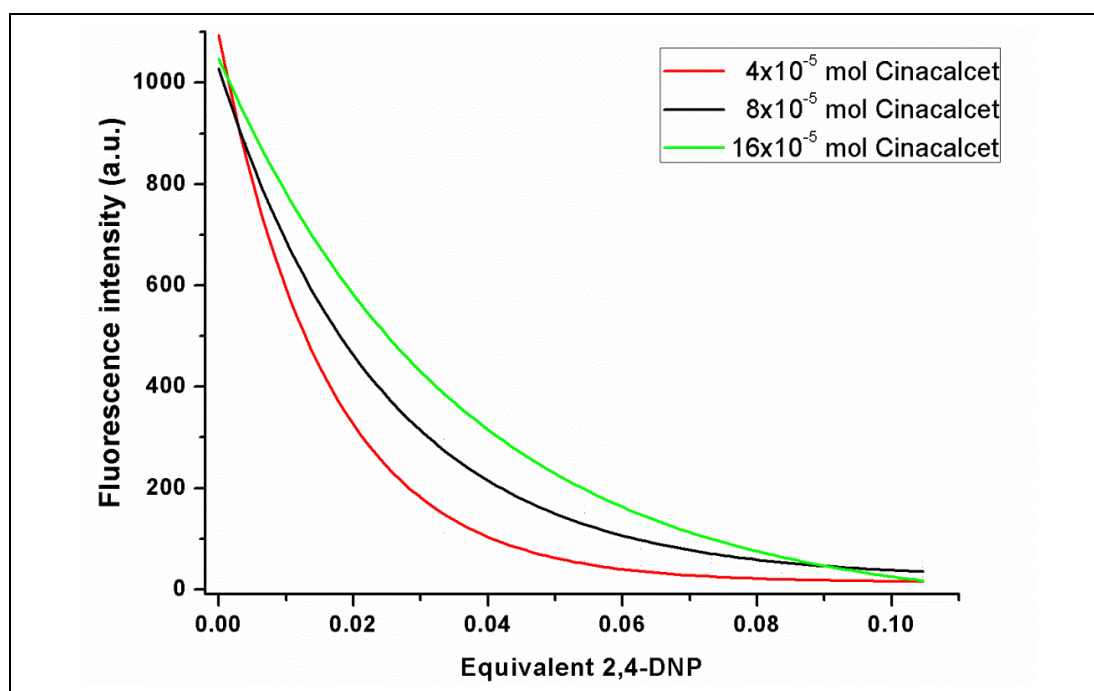


Figure 5.17: Binding behaviors of CIN-Gels (containing 0.04 mmol, 0.08 mmol and 0.16 mmol CIN) towards nitroaromatic compound 2, 4-DNP.

Flourescence properties of CIN-gel in different solvent also has been studied. Cin-Gel have presented high fluorecence intensity in all studied solvents. (Figure 5.18). ACN-Water (1:1) solvent system has been choosen due to optimum solubility of studied cations and nitroaromatic compounds.

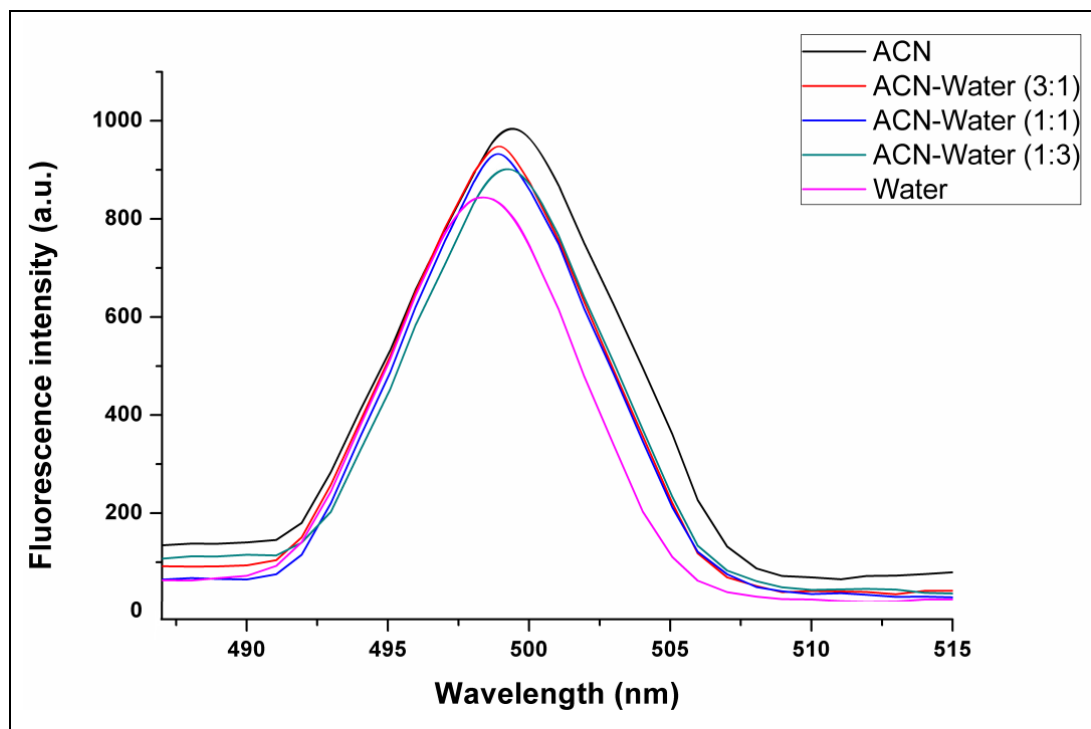


Figure 5.18: Fluorescence spectral responses of CIN-gel (containing 1.25×10^{-5} mol CIN) in ACN, water, ACN: water mixtures with different ratios v/v (3 : 1), (1 : 1) and (1 : 3) respectively.

The sensing and binding behavior of the cinacalcet labelled acrylamide hydrogel (CIN-gel) were measured for the detection of heavy metal ions and nitroaromatic compounds by fluorescence spectroscopy measurement. All the recognition experiments for metal cations and nitroaromatic compounds were performed in a mixed solvent system ACN:water (1:1, w/w) at 250 nm excitation wavelength (λ_{ex}) at room temperature. Cinacalcet fluorophore of CIN-gel depicted a strong emission spectrum in the absence of any heavy metal ions and nitroaromatic compounds due to photoinduced electron transfer or to exciplex formation from dialkylamine moiety (donor) to naphthalene moiety (acceptor). Related emission spectra and quenching efficiency for heavy metal ions are represented in Figure 5.19 and Figure 5.20 and for nitroaromatic compounds represented in Figure 5.21 and Figure 5.22.

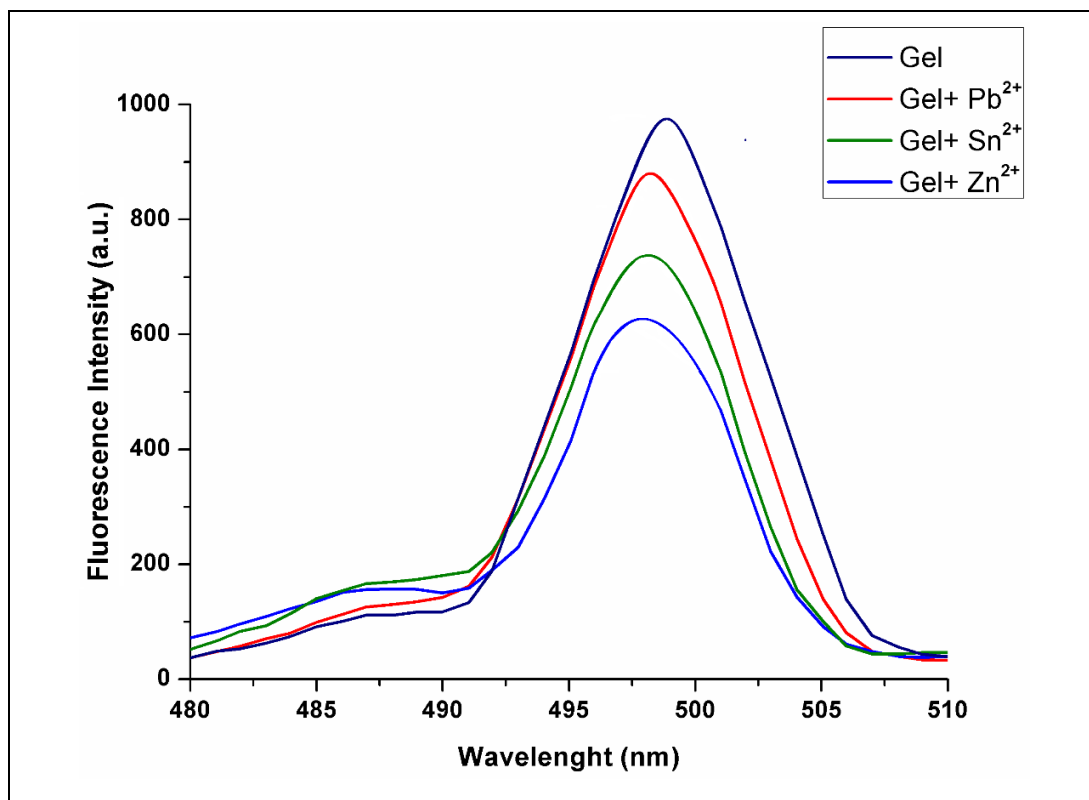


Figure 5.19: Fluorescence spectral response of CIN-gel (containing 1.25×10^{-5} mol CIN) in ACN:water (1:1, w/w) upon addition of 4.55 eq. of Pb^{2+} , Sn^{2+} and Zn^{2+} cations.

When CIN-gel was titrated with 4.55 equivalents of heavy metal ions (Sn^{2+} , Pb^{2+} , and Zn^{2+}) fluorescence emission of CIN-gel was quenched remarkably with slight blue-shifting of the band maxima (Figure 5.19). The stronger quenching ability of CIN-gel was related to photoinduced electron transfer from the excited CIN to nearby heavy metal ions which is a typical process in naphthalene derivatives or to exciplex formation [89].

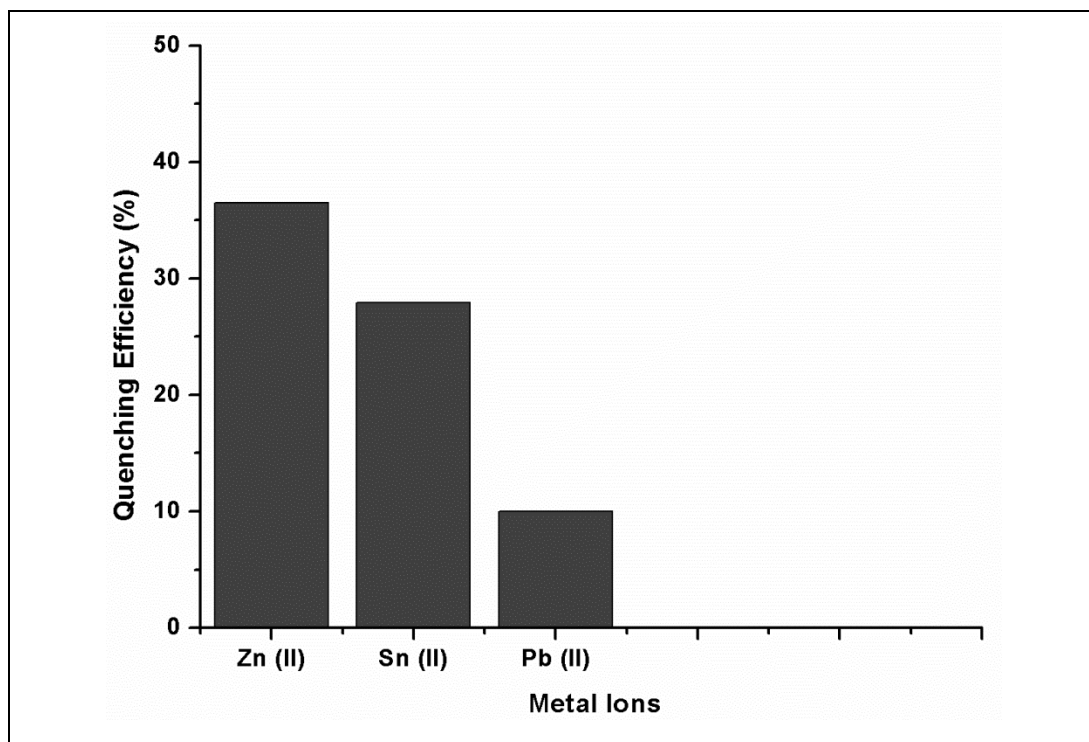


Figure 5.20: QE intensities of the CIN-gel upon adding of 4.5 eq. aimed heavy metal ions.

Quenching efficiency ratios (QE) of the metal cations were calculated and the obtained results were demonstrated in Figure 5.20. The highest QEs among the studied metal cations were observed for Zn^{2+} (35.93%). As shown in Figure 5.20, since other background metal cations (except for Sn^{2+} and Pb^{2+}) had small interferences for the fluorogenic determination, CIN-gel offered that could be used as a potential chemical probe for Zn^{2+} ion.

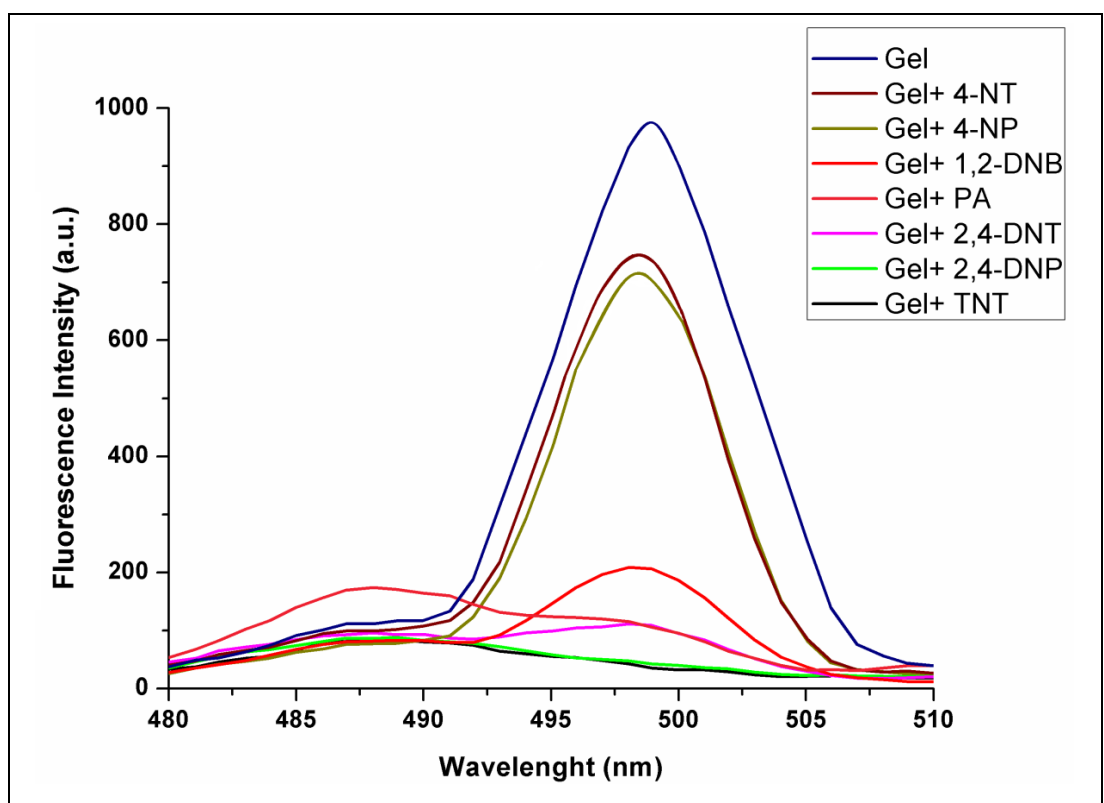


Figure 5.21: Fluorescence spectral response of CIN-gel (containing 1.25×10^{-5} mol CIN) in ACN:water (1:1, w/w) upon addition of 4.55 eq. of 4-NT, 4-NP, 1,2-DNB, 2,4-DNT, 2,4-DNP, PA and TNT.

When CIN-gel was titrated with 4.55 equivalents of nitroaromatic compounds (4-NT, 4-NP, 1,2-DNB, 2,4-DNT, 2,4-DNP, PA and TNT) fluorescence emission of CIN-gel was quenched remarkably with slight blue-shifting of the band maxima (Figure 5.21). The stronger quenching ability of CIN-gel was related to photoinduced electron transfer from the excited CIN to nitroaromatic compounds which is a typical process in naphthalene derivatives or to exciplex formation [89].

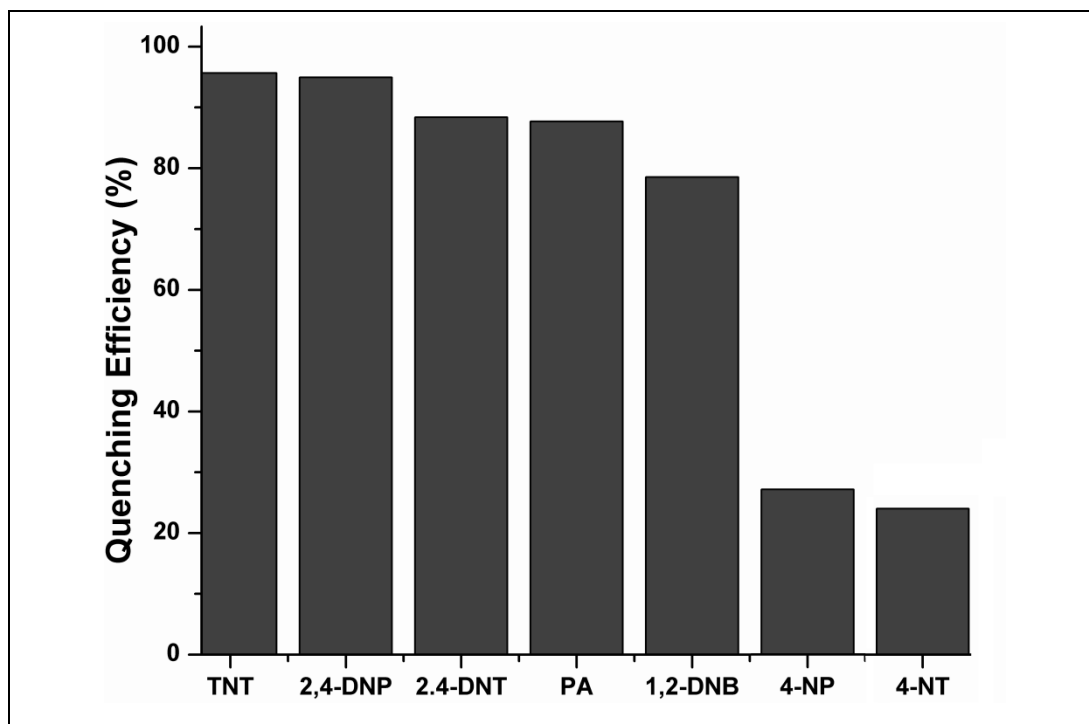


Figure 5.22: QE intensities of the CIN-gel upon adding of 4.5 eq. aimed nitroaromatic compounds.

Quenching efficiency ratios (QE) of the nitroaromatic compounds were calculated and the obtained results were demonstrated in Figure 5.22. The highest QEs among the studied nitroaromatic compounds were observed for TNT (95.67%) and 2,4-DNP (94.96%). As seen from Figure 5.22, since the interferences resulting from other compounds are not significant, CIN-gel offered that could be used as a potential chemical probe for TNT and 2,4-DNP.

The evolution of fluorescence emission spectra of CIN-gel upon titration with TNT at different equivalent ratios is depicted in Figure 5.23. The Stern–Volmer plot in the inset of Figure 5.23 suggests that the quenching process of CIN-gel by the addition of TNT is rather linear with the increasing concentration of the quencher. These results indicate a dynamic (collisional) quenching mechanism in which energy of the excited fluorophore was transferred nonradiatively to the quencher [53, 54]. Besides, the correlation coefficient were $R^2=0.99$, and the addition of TNT up to 4.55 eq for cinacalcet fluorophore of CIN-gel showed in Figure 5.23. According to these results, CIN-gel could be used for TNT sensing as fluorescence chemical probe.

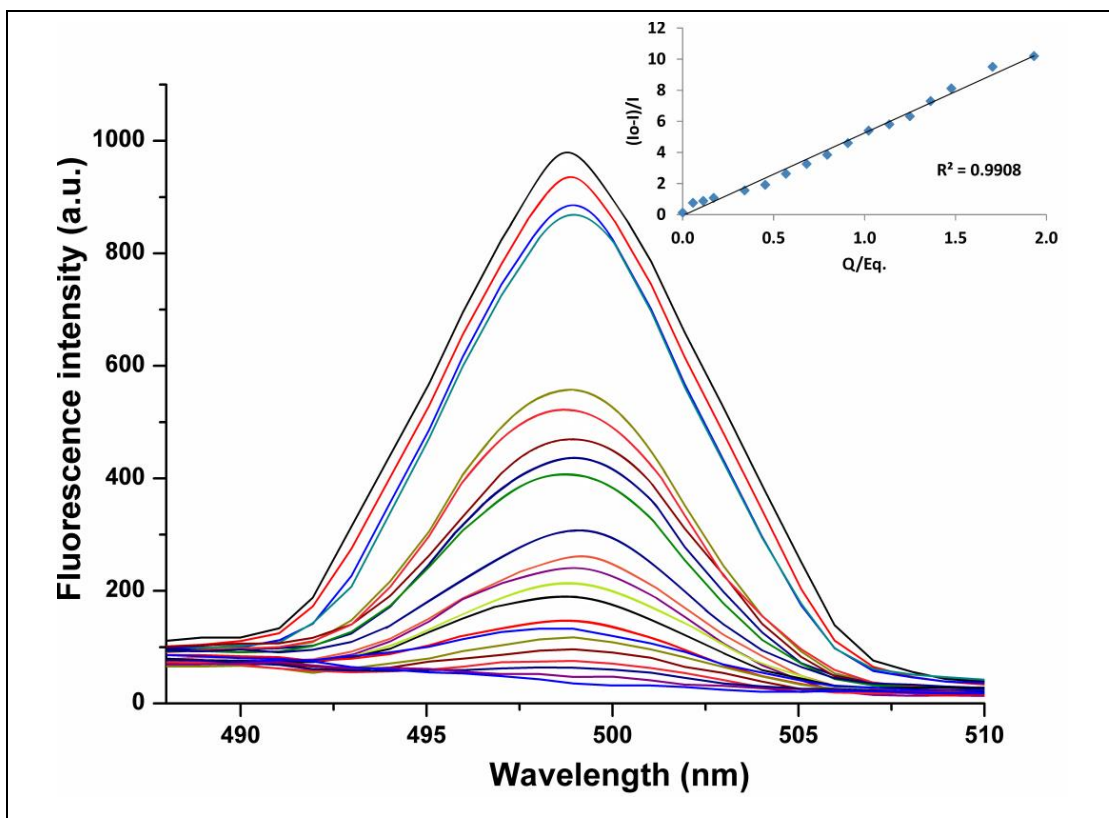


Figure 5.23: Fluorescence emission spectra of CIN-gel (containing 1.25×10^{-5} mol CIN) in ACN : water (1:1) in the presence of TNT at 0.06, 0.11, 0.17, 0.34, 0.45, 0.57, 0.68, 0.80, 0.91, 1.02, 1.14, 1.25, 1.36, 1.48, 1.70, 1.93, 2.05, 2.27, 2.50, 3.07 and 4.55 eq. ratios.

6. CONCLUSION

The dansyl fluorophore containing DNS-gel was prepared through photoinitiated free radical polymerization of acrylamide/*N,N'*-methylenebisacrylamide using dansyl chloride as a photoinitiator. The plausible photoinitiation mechanism was investigated by photobleaching, EPR and UV spectroscopies. Two possible initiation routes based on type I and type II systems were proposed. The successful synthesis of a dansyl containing hydrogel was also proved by SEM, fluorescence and UV spectroscopy. Subsequently, the obtained DNS-gel was utilized in fluorescence sensing application of various metal cations and nitroaromatic compounds. It is observed that fluorescence activities of DNS-gel were efficiently quenched after insertion of metal ions and nitroaromatic compound to the solution. The maximum QE for metal cations were monitored for Co^{2+} (72.56%) and DNS-gel linearly responded to the insertion of Co^{2+} ions till 50 equimolar. Interferences resulting from the presence of Cd^{2+} , Hg^{2+} , Pb^{2+} , Mn^{2+} , Ni^{2+} , and Zn^{2+} ions are negligible. The highest QEs for nitroaromatic compounds were observed for PA (88.55%) and 2,4-DNP (86.50%). And DNS-gel linearly responded to the insertion of PA till 0.1 equimolar. Therefore, DNS-gel has the potential to be used as an active fluorescent probe for the detection of Co^{2+} ion for metal cations and PA and 2,4-DNP for nitroaromatic compounds.

The cinacalcet functional CIN-gel was synthesized via photopolymerization of acrylamide/*N,N'*-methylenebisacrylamide (AAm/BAAm) by using cinacalcet chloride as photoinitiator. The SEM, UV-Vis, and fluorescence spectroscopy data verified the accomplished synthesis of the gel. Then, CIN-gel was used as fluorescence sensor probe for different metal cations and nitroaromatic compounds. Fluorescence emissions of CIN-gel were markedly quenched upon titration of metal cations and nitroaromatic compounds. The strongest QERs for metal cations and nitroaromatic compounds were observed for Zn^{2+} (35.93%), TNT (95.67%) and 2,4-DNP (94.96%), respectively. Also CIN-gel showed highly linear plot to the titration of TNT up to 4.55 equivalent. Therefore, CIN-gel as potentially chemical probe could be used as fluorescent sensor for the determination of Zn^{2+} cation for HMIs and TNT and 2,4-DNP for NACs.

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BIOGRAPHY

Mustafa UYGUN was born in 1985 in Istanbul, Turkey. He obtained his B.S. degree in Chemistry from Marmara University in 2008. Then, he obtained his master degree in Chemistry from Istanbul Technical University (GTU) in 2011. He then started his Ph.D. at the Graduate School of Natural and Applied Sciences in Gebze Technical University. His current research interests include polymer chemistry, photoinitiated radical polymerization, controlled polymerization techniques, “click” chemistry and fluorescence-active materials.

APPENDICES

Appendix A: Published Journals from Doctoral Thesis

Uygun M., Doganci E., Taşdelen M. A., Gurek A. G., (2018), “One-Pot Photoinduced Synthesis of Dansyl Containing Acylamide Hydrogels and Their Chemosensing Properties”, Journal of Applied Polymer Science, DOI: 10.1002/app.47096.