

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL

**CONSTRUCTION AND PHOTOCATALYTIC INVESTIGATION OF CADMIUM(II)
METAL-ORGANIC FRAMEWORKS BASED ON A CYCLOTRIPHOSPHAZENE
FUNCTIONALIZED HEXACARBOXYLATE AND DIVERGENT N-DONOR LIGANDS**

NIHAL KUZU

A THESIS OF MASTER OF SCIENCE
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THESIS SUPERVISOR: PROF. DR. YUNUS ZORLU

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T.C.
GEBZE TEKNİK ÜNİVERSİTESİ
LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

**SİKLOTRİFOSFAZEN FONKSİYONLU HEKZAKARBOKSİLAT VE FARKLI N-
DONÖR LİGANDLARA DAYALI KADMİYUM(II) METAL-ORGANİK KAFES
YAPILARIN OLUŞTURULMASI VE FOTOKATALİTİK İNCELENMESİ**

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SIGNATURE/SEAL

*To my
Lovely Family,
Cemalettin
Naciye
Hilal
Tarçın
Kimyon*

ABSTRACT

Global water pollution poses a severe ecological threat, adversely impacting human health, aquatic ecosystems, and biodiversity. Addressing the removal of colourants from wastewater is paramount, given their potential hazards to human well-being and the environment. The quest for effective and eco-friendly methods to eliminate colourants is of utmost significance. Conventional approaches such as adsorption, coagulation, and sedimentation have demonstrated inadequacies in removing colourants from wastewater, generating substantial residual breaks and necessitating additional disposal procedures. Advanced oxidation processes (AOPs), especially photocatalysis, have emerged as a promising strategy for efficiently eliminating diverse organic contaminants in wastewater.

This study investigates the synthesis, structure, and photocatalytic efficacy of novel Cd(II) MOFs, utilizing innovative cyclotriphosphazene/N-donor mixed ligands. Four Cd(II) MOFs, named **PCP-3**, **PCP-4**, **PCP-5**, and **PCP-6** (PCP denotes phosphazene-based coordination polymers), were synthesized and were investigated for their photocatalytic potential in removing a variety of dyes, including methylene blue (MB), methyl orange (MO), rhodamine B (RhB), and reactive orange 16 (RO16) from wastewater. Under UVA irradiation, the synthesized MOFs exhibit remarkable efficiency in degrading the selected dyes, exhibiting their potential in wastewater treatment. A mechanistic study explores the Cd(II) MOF's role in the photodegradation pathways, elucidating key intermediates and reaction mechanisms.

Additionally, this investigation explores the luminescence and optical properties of the MOFs, offering insights into their potential applications in optical devices and sensors. The PCPs demonstrated noteworthy photocatalytic activities in the degradation of MB, RhB, MO, and RO16 dyes, achieving up to 95% degradation efficiency within 40 to 60 minutes. The PCPs exhibited remarkable reusability and efficiency over five consecutive runs. The elucidation of the photocatalytic degradation mechanism identified $O_2^{\bullet-}$ and $\cdot OH$ as the primary reactive radicals. The PCP's superior photocatalytic activities depend on the N-donor type, positioning them as potential key photocatalysts for future research in environmental remediation. Characterization techniques, including X-ray crystallography, powder-XRD, TGA, FTIR, SEM-EDX, and UV-DRS measurements confirm the formation of Cd(II) MOFs with distinct binding modes between Cd(II) ions and cyclotriphosphazene linkers. This study contributes to understanding the synthesis and structure of PCPs, emphasizing their promising photocatalytic capabilities for diverse dye removal from wastewater. Insights into mechanistic aspects and exploration of luminescence/optical properties enhance the potential applications of these coordination polymers in environmental and optical fields.

Keywords: Photocatalysis, Organic Dye Removal, Coordination Polymer, Phosphazene, N-Donor.

ÖZET

Küresel su kirliliği, insan sağlığını, su ekosistemlerini ve biyolojik çeşitliliği olumsuz yönde etkileyen ciddi bir ekolojik tehdit oluşturmaktadır. İnsan sağlığına ve çevreye yönelik potansiyel tehlikeler göz önüne alındığında, renklendiricilerin atık sudan uzaklaştırılması çok önemlidir. Renklendiricilerin ortadan kaldırılmasına yönelik etkili ve çevre dostu yöntemlerin araştırılması son derece önemlidir. Adsorpsiyon, koagülasyon ve sedimantasyon gibi geleneksel yaklaşımlar, atık sulardan renklendiricilerin giderilmesinde yetersiz kalmakta, önemli derecede artık madde oluşmasına neden olmakta ve ek bertaraf prosedürleri gerektirmektedir. Gelişmiş oksidasyon işlemleri (AOP'ler), özellikle fotokataliz, atık sudaki çeşitli organik kirleticilerin etkin bir şekilde ortadan kaldırılması için umut verici bir strateji olarak ortaya çıkmıştır.

Bu çalışmada, siklotrifosfazen/N-donör karışık ligandlar kullanılarak yeni Cd(II) metal-organik kafes yapıların (MOF) sentezi, yapısı ve fotokatalitik etkinliği araştırılmıştır. **PCP-3**, **PCP-4**, **PCP-5** ve **PCP-6** (PCP, fosfazen bazlı koordinasyon polimerlerini ifade etmektedir) olmak üzere dört yenilikçi siklotrifosfazen/N-donör karışık ligand bazlı Cd(II) MOF'ları sentezlenmiştir. N-donör ligandlar olarak fenantrolin (phen), terpiridin (trp), 2,2'-bipiridin (2,2'-bpy) ve 4,4'-bipiridin (4,4'-bpy) kullanılarak sırasıyla **PCP-3**, **PCP-4**, **PCP-5** ve **PCP-6** koordinasyon polimerleri elde edilmiş ve metilen mavisi (MB), metil turuncu (MO), rodamin B (RhB) ve reaktif turuncu 16 (RO16) dahil olmak üzere çeşitli boyaların atık sudan uzaklaştırılması sırasında gösterdiği fotokatalitik potansiyel araştırılmıştır. UVA ışınlaması altında, MOF yapılar seçilen boyaların degradasyonunda dikkate değer bir verimlilik sergileyerek atık su arıtımındaki potansiyellerini ortaya koymuştur. Mekanistik bir çalışma, Cd(II) MOF yapılarının fotobozunma yollarındaki rolünü, anahtar ara maddeleri ve reaksiyon mekanizmalarını aydınlatmıştır.

Ek olarak, bu araştırma kafes yapıların lüminesansını ve optik özelliklerini inceleyerek bunların optik cihazlar ve sensörlerdeki potansiyel uygulamalarına dair bilgiler sunmuştur. PCP'ler MB, RhB, MO ve RO16 boyalarının bozunmasında kayda değer fotokatalitik aktiviteler sergileyerek 40 ila 60 dakika içinde %95'e varan bozunma verimliliği elde etmiştir. PCP'ler, ardı ardına yapılan beş denemede dikkate değer bir yeniden kullanılabilirlik ve verimlilik sergilemiştir. Fotokatalitik bozunma mekanizmasının aydınlatılması, $O_2^{\cdot-}$ ve $\bullet OH$ 'yi birincil reaktif radikaller olarak tanımladı. Sentezlenen PCP'ler N-donör tipine bağlı olarak üstün fotokatalitik aktiviteler sergileyerek, çevresel iyileştirme alanında gelecekteki araştırmalar için potansiyel anahtar fotokatalizörler olarak konumlandırılmaktadır. X-ışını kristalografisi, Toz-XRD, TGA, FTIR, SEM-EDX ve UV-DRS ölçümlerini içeren karakterizasyon teknikleri, Cd(II) iyonları ve siklotrifosfazen bağlayıcıları arasında farklı bağlanma modlarına sahip Cd(II) MOF'ların oluşumunu doğrulamıştır. Çalışma, siklotrifosfazen bazlı PCP'lerin sentezi ve yapısının anlaşılmasına katkıda bulunarak atık sudan çeşitli boyaların uzaklaştırılması için umut verici fotokatalitik yeteneklerini vurgulamaktadır. Mekanistik yönlerin anlaşılması ve lüminesans/optik özelliklerin araştırılması, bu koordinasyon polimerlerinin çevresel ve optik alanlardaki potansiyel uygulamalarını incelemiştir.

Anahtar Kelimeler: Fotokataliz, Organik Boya Giderimi, Koordinasyon

Polimeri, Fosfazen, N-Donör.

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LIST OF SYMBOLS AND ABBREVIATIONS

%	: Percent
°C	: The Degree Celsius
μL	: Microliter
•OH	: Hydroxyl Radical
1D	: One-dimensional
2D	: Two-dimensional
3D	: Three-dimensional
AOPs	: Advanced Oxidation Processes
bpy	: Bipyridine
BQ	: Benzoquinone
CB	: Conduction Band
CDCl ₃	: Deuterated Chloroform
CDs	: Cadmium Sulfide
CH ₂ Cl ₂	: Dichloromethane, DCM
CH ₃ CN	: Acetonitrile
CH ₄	: Methane
CHCl ₃	: Chloroform
cm	: Centimetre
CO ₂	: Carbon Dioxide
COD	: Chemical Oxygen Demand
CP	: Coordination Polymer
DHBD	: 3,4-dihydro-2H-1,2,4-benzothiadiazine-1,1-dioxide
DHQ	: 2,3-dihydroquinazolin-4(1H)-one
DEF	: Diethylformamide
DMA	: Dimethylacetamide
DMF	: Dimethylformamide
DMSO	: Dimethyl Sulfoxide
e ⁻	: Free Electron
ee	: Enantiomeric Excess
EDTA	: Ethylenediaminetetraacetic Acid
Eg	: Energy Gap
EG	: Ethylene Glycol
EtOH	: Ethanol
eV	: Electronvolt
Fe ₂ O ₃	: Iron (III) Oxide
FTIR	: Fourier Transform Infrared Spectroscopy
GTU	: Gebze Technical University
h ⁺	: Hole
H ⁺	: Hydrogen Ion
H ₂	: Molecular Hydrogen
H ₂ O	: Molecular Water
H ₂ O ₂	: Hydrogen Peroxide
H ₂ SO ₄	: Sulfuric Acid
HCl	: Hydrochloric Acid
HCPCP	: Hexakis(4-carboxylatophenoxy)cyclotriphosphazene
H-NMR	: Proton Nuclear Magnetic Resonance
HNO ₃	: Nitric Acid

Hz	: Hertz
IPA	: Isopropyl Alcohol
K	: Kelvin
kHz	: Kilo Hertz
K-M	: Kubelka-Munk
La	: Lantanite
LMCT	: Ligand-to-Metal Charge-Transfer
m	: Mass
M	: Molar
MALDI-TOF	: Matrix-assisted Laser Desorption/Ionization
Max	: Maximum
MB	: Methylene Blue
MeOH	: Methanol
mg	: Milligrams
MHz	: Megahertz
MIL	: Matériaux de l'Institut Lavoisier
min	: Minute
mL	: Millilitre
mmol	: Millimole
MO	: Methyl Orange
MOF	: Metal-Organic Framework
mW	: Milliwatt
N	: Nitrogen Atom
N ₂	: Molecular Nitrogen
NaOH	: Sodium Hydroxide
nm	: Nanometer
NMR	: Nuclear Magnetic Resonance
O	: Oxygen
O ₂	: Molecular Oxygen
O ₂ ^{•-}	: Superoxide Radical
O ₃	: Ozone
Oac	: Acetate
OH ⁻	: Hydroxyl Ion
P	: Phosphorus Atom
PCBs	: Polychlorinated Biphenyls
PCP	: Phosphazene-based Coordination Polymer
Pd(PPh ₃) ₄	: Tetrakis(triphenylphosphine)palladium(0)
pH	: Potential of Hydrogen/Power of Hydrogen
phen	: Phenanthroline
pK _a	: Acid Dissociation Constant
PMS	: Post Modern Synthesis
P-NMR	: Phosphorus Nuclear Magnetic Resonance
PXRD	: Powder Xray Diffraction
Q _{st}	: Isosteric Heat of Adsorption
RhB	: Rhodamine B
RO	: Reverse Osmosis
RO16	: Reactive Orange 16
ROS	: Reactive Oxygen Species
SBRs	: Sequential Batch Reactors
SBU	: Seconder Building Unit

SCN	: Thiocyanate
SCXRD	: Single-Crystal X-ray Diffraction
SEM-EDX	: Scanning Electron Microscopy - Energy Dispersive X-ray
terp	: Terpyridine
TGA	: Thermal Gravimetric Analysis
TiO ₂	: Titanium Dioxide
TIP	: Triisopropyl Phosphite
UiO	: University of Oslo
UV	: Ultraviolet
UV-DRS	: UV-Diffuse Reflectance Spectroscopy
VB	: Valence Bond
VOCs	: Volatile Organic Compounds
VUV	: Vacuum Ultraviolet
WO ₃	: Tungsten Trioxide
XRD	: X-ray Diffraction
ZIF	: Zeolitic Imidazolate Framework
Zn(OH) ₂	: Zinc Hydroxide
ZnO	: Zinc Oxide
ZnS	: Zinc Sulfide
λ_{max}	: Maximum Absorption Wavelength

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1. INTRODUCTION

Water is the primary constituent that comprises the fundamental structure of all living organisms and ecosystems. In order to maintain the overall equilibrium, it is imperative to have a substantial quantity of uncontaminated water that is readily available. Nevertheless, the problem of water contamination persists as a consequence of the growing human population and the rapid progress of industrialization. Water pollution refers to the degradation of water quality caused by the introduction of dangerous substances into water sources and insufficient treatment procedures. Water contamination arises from the amalgamation of industrial waste, agricultural chemicals, home trash, and diverse pollutants. With each passing day, the significance of the issue grows as pollutants become resistant to effective purification procedures [1].

Wastewater can contain a diverse range of contaminants originating from home and industrial origins. These pollutants can typically arise from organic substances, inorganic substances, physical substances, and chemical compounds. Organic dyes, which fall under the category of chemical compounds, offer a significant and hazardous threat among the different pollutants generated by water pollution. Dyes, particularly those employed in sectors such as textile, leather, and paper, generate chemical contamination when combined with wastewater. These dyes have the ability to alter the color of water and can pose a threat to the environment. Certain dyestuffs include poisonous and carcinogenic characteristics, hence necessitating treatment before being discharged into water sources. The introduction of dyestuffs into water can have detrimental impacts on ecosystems and diminish the water's utility [2].

The efficient elimination of dyestuffs from wastewater is crucial for safeguarding the industrial establishments must enhance environment and ensuring human well-being. Consequently, industrial establishments must enhance their wastewater treatment systems and embrace sustainable treatment technologies. Wastewater is treated using physical, chemical, and biological processes as well as modern technologies to eliminate dyestuffs. Physical treatment procedures encompass coagulation, flocculation, and filtering, whereas chemical treatment methods involve oxidation and

adsorption. Oxidation facilitates the chemical breakdown of dyestuffs through the use of oxidation agents like O_3 , Cl^- , or H_2O_2 . On the other hand, adsorption involves extracting dyestuffs from water by employing substances such as activated carbon, bentonite, or zeolite. Biological treatment methods encompass techniques that involve the utilization of microorganisms and phytoremediation. Furthermore, the utilization of modern treatment methods, including reverse osmosis, photocatalytic oxidation, and electrochemical treatment, is crucial for efficiently eliminating dyes [3].

Aside from the harm inflicted by dyes on water resources, aquatic ecosystems, and human well-being, the management of water treatment, waste control, and treatment expenses are of utmost significance. The limitations of existing procedures have prompted the exploration of other methods, such as AOPs. Among them, photocatalysis has emerged as a highly effective option for eliminating organic contaminants from wastewater. CPs are becoming increasingly important in the field of photocatalysis due to their distinct features, which have the capacity to enhance photocatalytic efficiency [4]. This study aims to synthesize and investigate the photocatalytic capabilities of CPs. It specifically focuses on novel Cd(II) MOFs based on cyclotriphosphazene/N-donor mixed ligands. These MOFs are significant because they offer sites for binding organic contaminants and enable effective charge transfer in the photocatalytic process. This makes them highly promising for environmental applications [4].

The research is centered on investigating the process of photocatalytic degradation of organic dyes, specifically focusing on methylene blue as a sample example. The characterization process will involve the utilization of many techniques, including SCXRD, TGA, FTIR a thorough investigation will be conducted on the luminescence and optical characteristics of the synthesized CPs. This analysis will offer valuable insights into the adaptability of these materials for various applications, including improved optical devices, in addition to photocatalysis [4].

Water pollution results in the contamination of water resources as a consequence of diverse sources, including industrial activity, agricultural practices, and improper waste disposal. These pollutants pose a hazard to marine life and have significant implications for human health. Lately, there has been a concentrated effort in research to create novel and efficient techniques for eliminating pollutants from water

contamination. An encouraging method involves utilizing carboxylate-based MOFs as efficient catalysts for photocatalysis [4]. MOFs are a type of porous hybrid materials that are formed by the bonding of metal ions or clusters with organic ligands. These frameworks are well-suited for water purification applications due to their adjustable internal structures, high porosity, crystallinity, and extensive surface areas [4]. Carboxylate-based MOFs show significant promise as highly efficient photocatalysts for breaking down organic dyes in water settings [4]. By introducing metals and nanoparticles into carboxylate-based MOFs, their photocatalytic activity is enhanced, allowing them to efficiently remove various contaminants [4].

The objective of this thesis is to address the issue of eliminating organic dyes from wastewater by MOF-based photocatalysts. This research aims to contribute to the creation of versatile materials that may be used in a wide range of applications, from environmental remediation to sophisticated technology. It does so by carefully examining and combining different aspects. The master's thesis examines the process of creating and studying carboxylate-based MOF structures, with a focus on their effectiveness in using light to break down dyes. The exploration will examine optimization strategies for the synthesis of MOFs, showcase different analytical techniques employed in characterisation, and evaluate the effectiveness of carboxylate-based MOFs in removing dyes. The main goal is to provide knowledge on the design and use of these MOFs, offering answers to important issues like water pollution, treatment of industrial effluent, and environmental pollution. Evaluating the photocatalytic characteristics will highlight the capacity of MOF technology as a viable and eco-friendly method for reducing the environmental consequences of dyes. This thesis aims to make a significant contribution to environmental sustainability by combining environmental engineering and nanotechnology. It seeks to identify future research opportunities and establish MOF technology as a crucial factor in reducing the environmental impact and promoting a more sustainable future.

2. WATER TREATMENT

The objective of water treatment is to eliminate detrimental impurities and pollutants from the wastewater prior to its discharge into the environment. The objective of this treatment procedure is to decrease the toxicity, chemical oxygen demand, color, and concentration of organic and inorganic substances to levels that are considered acceptable. This helps to minimize the negative effects of industrial waste on the environment and ensures the protection of aquatic ecosystems and human health. Furthermore, it guarantees that the wastewater complies with regulatory norms and conditions for discharge [4].

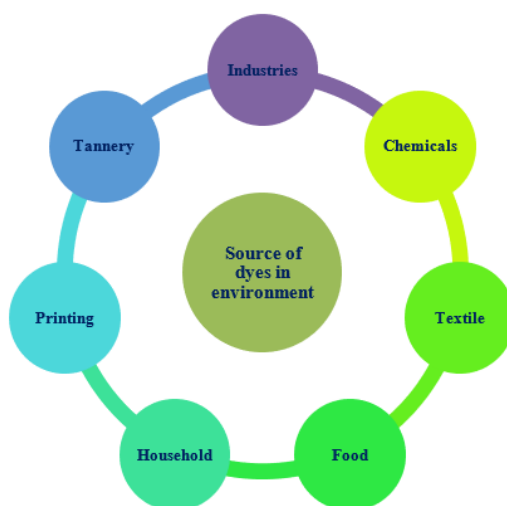


Figure 2.1: Source of dyes in the environment [4].

Every treatment approach is subject to several limitations, such as expenses, viability, effectiveness, practicality, dependability, ecological consequences, sludge generation, operational complexity, pre-treatment prerequisites, and the potential creation of harmful by-products. However, only a limited number of treatment techniques are typically used by the industrial sector for wastewater treatment, mostly due to technological and economic factors. In general, the elimination of pollutants from effluents is accomplished using physicochemical and/or biological methods. Current research is dedicated to finding more economical combinations of systems or exploring new options. Below are explanations of various water purifying techniques:

2.1. Treatment Techniques of Dye in Wastewater

2.1.1 Physical Methods

Physical techniques for eliminating dye from wastewater involve a range of technologies that utilize physical characteristics to remove pollutants without modifying their chemical composition. They are highly efficient in purifying wastewater that contains high levels of suspended solids and dye particles. Nevertheless, the effectiveness of these procedures can be modified by variables such as the nature and strength of the dye, the existence of additional impurities, and operational factors like temperature and pH. In addition, physical techniques usually necessitate pre-treatment or post-treatment steps to achieve full removal of colors, and they may not be efficient for dyes that are extremely soluble or chemically stable [5].

Adsorption Method

The adsorption method is a commonly employed and efficient technology for treating wastewater containing dyes. It utilizes the large surface area and porous nature of adsorbent materials to eliminate pollutants. This technique is based on the non-chemical, physical attraction between dye molecules and the surface of the adsorbent. This attraction is usually due to van der Waals forces or electrostatic interactions. Activated carbon, clay minerals, and biomass-derived materials are commonly used as adsorbents. These materials are chosen based on their cost-effectiveness, availability, and ability to adsorb substances. The process entails the adsorption of dye molecules onto the surface of the adsorbent, resulting in a decrease in the concentration of dye in the effluent. The efficiency of the adsorption process is highly influenced by parameters such as pH, temperature, contact time, and adsorbent dose. Physical adsorption offers several benefits, such as its straightforwardness, simplicity in operation, and the potential for regenerating and reusing the adsorbent. These characteristics make it an environmentally friendly option for treating wastewater. In addition, physical adsorption could eliminate a wide range of dyes, including those that are resistant to biodegradation and other forms of treatment. Nevertheless, certain obstacles, such as the saturation of adsorbent sites, the proper disposal of used adsorbents, and the requirement for pre-treatment to improve the effectiveness of adsorption, hinder the removal of a wide range of dyes, including those that require attention [5].

Membrane Technology

Physical membrane technology refers to a range of treatment methods used to eliminate colors from wastewater. This is important since dyes have a long-lasting negative effect on the environment. Ultrafiltration utilizes semi-permeable membranes to segregate dye molecules according to their size, thereby eliminating bigger dye particles and colloids through size exclusion. Nanofiltration, which operates at a smaller scale, effectively filters dyes by precisely targeting their molecular weight and charge. This process significantly improves the removal of both organic and inorganic pollutants. RO is a process that uses high pressure to push water through a tightly packed membrane. This process effectively removes dye by filtering out particles based on their size and charge, resulting in clean water. In addition, membrane distillation aids in the removal of dyes by evaporating water across a hydrophobic membrane, leaving impurities behind. On the other hand, electrodialysis utilizes ion-exchange membranes to separate charged dye particles, hence improving the purifying procedures. Each technique provides unique benefits in terms of dye removal efficiency, scalability, and operational practicality, which can meet different requirements for wastewater treatment. By combining membrane technology with processes like adsorption or oxidation, the efficiency of dye removal is improved, effectively tackling the difficulties presented by wastewater containing dyes. Therefore, comprehending and enhancing these physical membrane technologies are crucial for sustainable water management, guaranteeing less environmental contamination and enhanced water quality in industrial and municipal environments [5].

High-pressure procedures such as RO necessitate a substantial amount of energy input, resulting in higher operational expenses. The efficiency of the membrane is reduced, and operational expenses are increased due to the accumulation of dyes and other pollutants on its surface, which leads to membrane fouling and requires frequent cleaning or replacement. Moreover, the proper disposal of highly concentrated dye solutions and cleaning chemicals utilized in membrane maintenance presents difficulties concerning their environmental consequences [5].

2.1.2 Biological Methods

Biological techniques for treating wastewater tainted with dye entail utilizing live organisms or their biochemical processes to break down or eliminate dye contaminants. The challenges arise from the slow degradation rates and incomplete elimination of some dye types, which often necessitate longer treatment times or additional processes. Moreover, the efficacy of biological treatments might be influenced by the unique dye composition and properties of the wastewater, which restricts their widespread applicability. In addition, the expansion of biological treatment systems for industrial wastewater can be intricate and expensive, necessitating meticulous control of operational parameters to ensure consistent performance. Therefore, it is essential to enhance the effectiveness of biological methods for treating dye wastewater by developing advanced technologies and using integrated approaches [6].

Aerobic Process

Aerobic biological treatment methods employ oxygen-dependent bacteria to break down pigments found in wastewater. These processes commonly take place in aerobic bioreactors or activated sludge systems, where microorganisms catalyze the oxidation of organic pollutants, such as colors, into less hazardous chemicals, such as CO₂ and H₂O. The advantages of this method are its great efficacy in removing dyes and its versatility in treating a wide variety of dye types. Nevertheless, aerobic processes necessitate a substantial amount of energy for aeration, resulting in high operational costs. Additionally, they are responsive to changes in pH and temperature, which might impact the activity of microorganisms and the effectiveness of the treatment process. Additionally, the sludge produced during the process necessitates appropriate disposal or additional treatment because of its possible toxicity and elevated organic content [6].

Anaerobic Process

Microorganisms that function in the absence of oxygen to decompose organic compounds, including pigments, into simpler forms such as CH₄ and CO₂, are the subject of anaerobic treatment methods. In comparison to aerobic methods, anaerobic digestion can take place in anaerobic bioreactors or lagoons, which provide benefits

such as the potential for CH₄ production as a byproduct and reduced energy consumption. Nevertheless, anaerobic processes are generally slower at degrading dyes than aerobic processes. Additionally, they are less effective in treating specific types of pigments that are highly resistant to biological degradation. Furthermore, anaerobic systems are susceptible to fluctuations in pH and noxious substances, which can impede microbial activity and diminish the efficacy of treatment [6].

Sequential Batch Reactors (SBRs)

SBRs integrate anaerobic and aerobic processes in a single system, enabling the sequential treatment of wastewater. This strategy provides benefits such as increased adaptability in treating different amounts of dyes and higher overall efficiency by utilizing both forms of microbial metabolism. Nevertheless, SBRs necessitate meticulous regulation of operating parameters and lengthier treatment durations in comparison to single-stage aerobic systems. Furthermore, they require additional infrastructure and operational complexity, resulting in higher original investment and maintenance expenses. Moreover, effectively handling the shift from anaerobic to aerobic circumstances can be difficult and may result in less-than-optimal treatment outcomes if not adequately regulated [6,7].

2.1.3 Chemical Methods

Chemical approaches used to treat dyes in wastewater encompass a range of procedures that target the elimination or breakdown of dye contaminants. Coagulation and flocculation are often employed methods in which chemicals such as alum or ferric chloride are introduced to create flocs that ensnare dyes, which are subsequently eliminated through sedimentation or filtration. The utilization of coagulation and flocculation techniques involves the adjustment of pH to induce the precipitation of dyes as insoluble complexes, which are then separated. Although chemical techniques are efficient, they have significant drawbacks. Frequently, substantial quantities of chemicals are necessary, resulting in elevated operational expenses and the possibility of environmental consequences arising from chemical remnants. Furthermore, the sludge produced during the treatment process might provide challenges in terms of management and may necessitate additional treatment or disposal, hence increasing the total complexity and cost of the operation. Moreover, certain chemicals employed

management and may necessitate additional treatment or disposal, hence increasing the total complexity and cost of the operation. Moreover, certain chemicals employed in these procedures have the potential to produce detrimental by-products or present health hazards if not handled appropriately. Moreover, the effectiveness of chemical treatments may differ based on variables such as the specific dye used, the makeup of the wastewater, and the parameters of the treatment process. Therefore, it is crucial to meticulously optimize and monitor these elements to consistently obtain desired outcomes. Chemical technologies provide strong solutions for treating dye wastewater, but their limitations emphasize the importance of exploring alternate or supplementary approaches to achieve sustainable and efficient rehabilitation [7].

Oxidation methods, such as ozonation or AOPs using O_3 or UV light, degrade dyes into non-toxic compounds. AOPs are particularly successful in achieving total mineralization of stubborn organic pollutants and ensuring comprehensive disinfection. This makes them superior to conventional methods for treating a diverse range of contaminants that are resistant to typical approaches [7].

Table 2.1: Advantages and disadvantages of the main conventional methods used for the treatment of polluted industrial wastewater[7].

Methods	Classification	Technical Essential	Importance	Scope of Applications	Disadvantages
Physical	Adsorption method	Employs adsorbents (e.g., activated carbon) to eliminate contaminants by adhering them to the surface.	Waste utilization, simple operation	Water soluble dyes, cationic dyes	The necessity for periodic regeneration or replacement of adsorbents and high operational costs.
	Membrane technology	Utilizes semi-permeable membranes to separate contaminants from water according to their size and charge.	The decolorization effect is obvious	Disperse dyes, desalination, wastewater reclamation, and ultrapure water production.	include the high initial setup costs, membrane contamination, and high energy consumption.
Biological	Aerobic Method	In the presence of oxygen, aerobic microorganisms are employed to decompose organic matter.	Economy	Primarily employed in industries with a high organic load and municipal effluent treatment.	Long processing time, unstable effect, impact resistance
	Anaerobic Process	Utilizes anaerobic microorganisms to decompose organic matter in the absence of oxygen.	Decolorization effect is good, residence time is short	Suitable for the treatment of high-strength wastewater, including that produced during the processing of food and sediment.	Produce a large amount of aniline, the effluent biological toxicity increased
	Anaerobic/Aerobic Process	Sequences of both anaerobic and aerobic processes to optimize pollutant degradation.	High COD removal rate, good economy	Employed in wastewater treatment processes that are intricate, including industrial effluents and landfill discharge.	Poor impact resistance, poor adaptability, reaction time
Chemical	Coagulation and Flocculation	Utilizes coagulants to form larger aggregates by clumping particles together.	Highly effective in the removal of suspended solids and reduction of turbidity.	Disperse dyes, vat dyes, sulphur dyes	Low decolorization ability for hydrophilic dyes, low COD removal efficiency, chemical sludge production, secondary pollution
	Neutralization	pH is adjusted to a neutral range by utilizing acids or bases.	Simple and crucial for maintaining stable treatment conditions.	Essential for all wastewater with highly acidic or alkaline pH levels.	Requires precise management to prevent excessive correction.
	Precipitation	This process is crucial as it transforms dissolved metals and phosphates into forms that are no longer soluble.	Highly effective in the removal of heavy metals and phosphates.	Suitable for wastewater containing high concentrations of metals.	Generates sludge containing metals that need to be disposed of safely.
	Adsorption	Utilizes adsorbents such as activated carbon to effectively capture pollutants.	Extremely effective in eliminating leftover dyes and trace organic substances.	Suitable for polishing treated wastewater.	High cost, unsatisfactory COD removal rate
	Ion Exchange	Facilitates the exchange of ions in the water with ions on a resin.	Effectively eliminates targeted ions such as heavy metals and nitrates.	Perfect for effectively removing contaminants present in low concentrations.	The capacity for ion exchange is limited and the operational costs are high.

Advanced Oxidation Processes (AOPs)

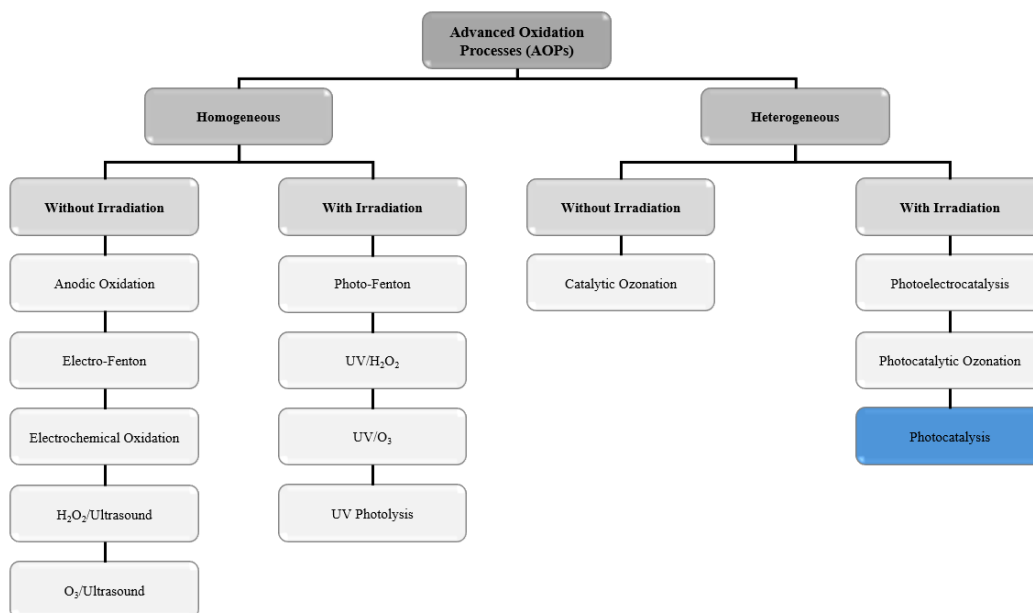


Figure 2.2: Advanced oxidation process diagram [8].

AOPs are innovative methods that effectively break down stubborn organic molecules in wastewater by producing $\bullet\text{OH}$ using a mix of UV irradiation, catalysts, and oxidants. Originally introduced for the treatment of drinking water in the 1980s, AOPs have subsequently been utilized in many wastewater treatment situations due to their ability to effectively break down complex aromatic compounds and stubborn colours that traditional technologies have difficulty decomposing. AOPs offer significant benefits for dealing with non-biodegradable contaminants and pathogens that are resistant to conventional treatment methods. The process entails the swift generation of $\bullet\text{OH}$ radicals, which are extremely reactive and have the ability to oxidize organic pollutants into mineral salts, water, and CO_2 . Nevertheless, despite their effectiveness, AOPs pose difficulties such as substantial operational expenses, mostly owing to energy demands and the necessity for catalysts and oxidants. In addition, the unselective characteristics of $\bullet\text{OH}$ radicals can might result in the creation of potentially hazardous by-products if not appropriately controlled. Although AOPs provide substantial advantages in terms of efficient pollutant removal and potential toxicity reduction, their incorporation into wastewater treatment systems necessitates careful evaluation of cost-effectiveness and environmental consequences. In many cases, biological treatments are favored for the final stages of dye degradation and mineralization [8].

Recently, the use of photochemical and catalytic technologies in chemical water treatment has resulted in notable advancements in the process of oxidizing and breaking down organic molecules in water. AOPs serve as contemporary alternatives to conventional water treatment methods. AOPs primarily generate transient oxygenated molecules, such as $\text{OH}\cdot$ and $\text{O}_2^{\cdot-}$. The $\text{OH}\cdot$, renowned for its exceptional reactivity and absence of selectivity, can be readily produced and utilized in these procedures. Conventional oxidizing agents, such as H_2O_2 and O_3 , are utilized in combination with stimuli like UV light to produce these reactive compounds. This procedure facilitates the oxidation of resilient organic compounds and pesticides that are challenging to handle using traditional methods. Notable AOPs comprise reactive species and VUV techniques [8].

Homogeneous Processes

Homogeneous: In most cases, the catalyst is in the same phase as the reactants, which is typically in solution. Light has the ability to accelerate reactions that result in the breakdown of pollutants [8].

Heterogeneous Processes

Heterogeneous reactions on light-activated catalysts, such as TiO_2 , occur when organic molecules decompose upon exposure to UV light, without depleting the catalyst. First identified by Carey and his team in 1976, TiO_2 has the ability to break down contaminants like polychlorinated biphenyls (PCBs) in water. The process entails the absorption of UV radiation by TiO_2 , resulting in the generation of excited e^-/h^+ . These excited particles then produce reactive species, such as $\cdot\text{OH}$, which oxidize and decompose organic contaminants. Nevertheless, this approach is constrained by the requirement for organic molecules to cling to the surface of TiO_2 and the relatively poor efficacy in generating $\cdot\text{OH}$. This procedure, which is not categorized as an AOP, can be improved by the addition of O_3 and can employ different light sources, such as solar energy, to activate TiO_2 for environmental purposes [8].

2.2. Photocatalytic Reactions and Catalysts

A novel approach to water treatment involves the photo-induced degradation of organic pollutants. The term "photocatalysis" combines "photo," meaning light, and "catalysis." Catalysis refers to a process where a substance accelerates a chemical reaction by lowering the activation energy without being consumed or altered at the end of the reaction. Photocatalysis, therefore, is a reaction that uses light (photons) to activate a substance (photocatalyst) which in turn modifies the rate of a chemical reaction without being consumed in the process [8,9].

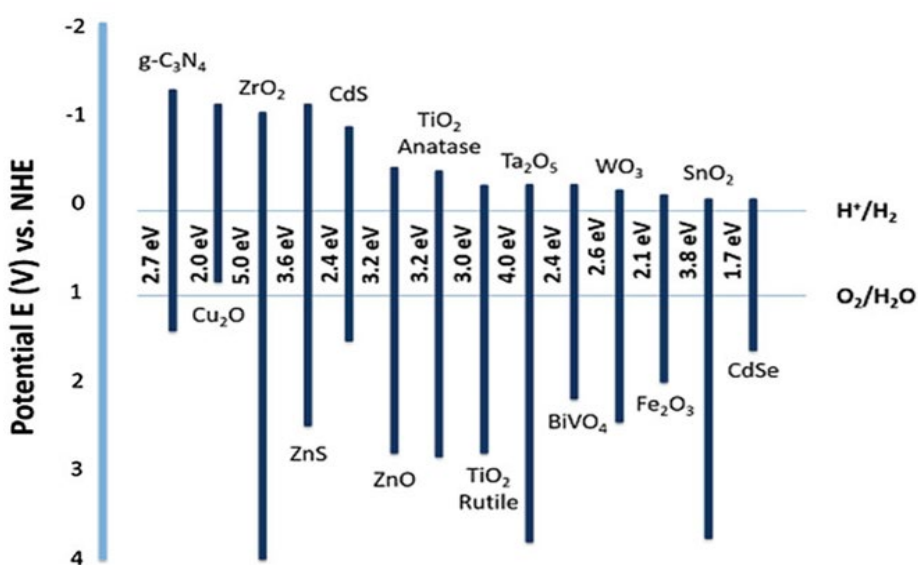


Figure 2.3: Various band structures of semiconductors with the redox potentials for water treatment [9].

Photocatalysis is a process that uses photocatalysts to drive chemical reactions with photons. Typically, these photocatalysts are metal oxide semiconductors like TiO₂ or ZnO, known for their high photocatalytic activity. When exposed to light energy, these materials activate reactants on their surfaces, enabling energy transfer through the movement of charge carriers. This process forms e^-/h^+ pairs, with electrons moving to the conduction band and holes remaining in the valence band. These pairs are essential for catalyzing the desired reactions. Photocatalysis is applied in various fields such as wastewater treatment, air purification, and solar energy conversion due to its ability to degrade and mineralize organic pollutants in water. The light energy absorbed by the photocatalyst creates e^-/h^+ pairs that migrate across the catalyst's surface. Electrons drive oxidation reactions, while holes participate in reduction reactions, forming

highly reactive species like superoxide and $\bullet\text{OH}$, which degrade organic pollutants efficiently [9].

Photocatalysis holds substantial promise in various industries, including automotive, construction, consumer products, energy, environmental, mechanical/chemical, and medical/dental. Considerable research has been dedicated to TiO_2 and ZnO because of their exceptional effectiveness in the presence of UV radiation and their ability to withstand corrosion. Scientists are also investigating alternative materials and techniques to enhance the efficiency of photocatalysis for different uses. Photocatalysis aims to improve operational performance and tackle issues in wastewater treatment in the future. Photocatalysis is a process that happens on the surface of metal oxide semiconductors when they are exposed to light radiation. This process creates pairs of electrons and holes, which then participate in oxidation and reduction reactions. These reactions produce reactive species that can break down organic contaminants. This method is environmentally friendly and sustainable, as it eliminates the use of dangerous chemicals and prevents the production of hazardous by-products. It has the ability to efficiently break down a wide variety of organic contaminants, such as dyes, pesticides, medicines, and VOCs. It is adaptable for treating both air and water. Photocatalysis is an economically efficient process that makes use of readily available and low-cost ingredients such as TiO_2 and ZnO . It can also be easily incorporated into current infrastructure, making it well-suited for industrial use. Researchers are currently addressing the difficulty of generating high photocatalytic efficiency under visible light by exploring methods such as doping photocatalysts with different elements or altering their surface patterns to enhance absorption in the visible spectrum. The range of values is from 6 to 9, inclusive [9].

In recent years, the field of photocatalysis has garnered increasing attention. Photocatalysis involves using catalysts to drive chemical reactions through light energy absorption, with photocatalysts being specific catalysts that harness photons to activate these reactions. On the surface of metal oxide semiconductors like TiO_2 and ZnO , photocatalytic reactions occur when exposed to light. These semiconductors absorb electromagnetic wavelengths, generating e^-/h^+ pairs. The electrons and holes migrate to different parts of the catalyst's surface, where the electrons induce oxidation reactions, and the holes facilitate reduction reactions [9].

Photocatalytic reactions are vital in water treatment processes, where they decompose H_2O to produce $\bullet\text{OH}$ and H_2 [9]. This process involves forming superoxide and $\bullet\text{OH}$, which degrade pollutants in wastewater. Therefore, photocatalytic reactions are instrumental in environmental remediation and water treatment. The efficiency of these reactions in breaking down organic pollutants and mineralizing water underscores their value.

In essence, photocatalytic reactions, driven by metal oxide semiconductors such as TiO_2 and ZnO , involve the activation of reactants through light energy absorption and the subsequent generation of e^-/h^+ pairs. These pairs initiate oxidation and reduction reactions, leading to organic pollutants and water mineralization degradation.

Photocatalysis mirrors the natural process of photosynthesis in plants, which is driven by chlorophyll, a natural photocatalyst. In artificial systems, when a semiconductor (serving as the photocatalyst) is irradiated with light energy greater than its band-gap energy ($h\nu > E_g$), e^- are excited from the valence band (VB) to the conduction band (CB). This excitation leaves behind photogenerated holes (h^+) in the VB. The e^-/h^+ then migrate to the surface of the semiconductor, where they participate in redox reactions.

The photogenerated electrons and holes on the semiconductor surface can react with water and O_2 to form highly reactive species such as $\bullet\text{OH}$ and $\text{O}_2^{\bullet-}$. These ROS can effectively oxidize and break down a wide range of organic pollutants into harmless end-products like CO_2 and water. A semiconductor photocatalyst typically comprises the component: the photoharvester-catalyst. The integration of catalysts with the semiconductor property enhances charge transfer and reduces charge recombination. Photocatalytic degradation of pollutants in water is primarily facilitated by a series of oxidative-reductive chain reactions occurring at the photo-activated surface. The general mechanism can be outlined as follows [9]:

The photocatalytic degradation reaction typically involves three main active species: $\text{OH}^\bullet$, h^+ , and $\text{O}_2^{\bullet-}$. Among these, $\text{OH}^\bullet$ radicals are the primary oxidants in the photocatalytic degradation of pollutants in aqueous solutions. The generation of $\text{OH}^\bullet$ radicals generally occurs via two routes:

1. H_2O and OH^- in the water environment are readily oxidized by photogenerated h^+ to form $\text{OH}^\bullet$ radicals (equations 2 & 3).
2. O_2 present in the aqueous solution is reduced by photogenerated e^- to form $\text{O}_2^{\bullet-}$ radicals (equation 5), which then react with H^+ to form $\text{OOH}^\bullet$ radicals (equation 6) and subsequently decompose to produce $\text{OH}^\bullet$ radicals (equations 7, 8, and 9).

Moreover, the photogenerated h^+ is widely considered an oxidant for directly degrading organic contaminants, with its capacity depending on the catalyst type and oxidation conditions. The efficiency of photocatalytic degradation of pollutants is influenced by various parameters such as dye concentration, pH of the dye solution and catalyst, temperature, oxidizing agents, dopant content, and catalyst loading. Additionally, selecting an appropriate light source is crucial for the different types of catalysts used. Therefore, investigating various reaction conditions is essential to gain insights for achieving better photocatalytic performance.

Photocatalysis offers several advantages over traditional water treatment methods:

1. Efficiency: Photocatalysis can degrade a wide range of organic pollutants, including those that are resistant to conventional treatments.
2. Eco-Friendly: The process results in harmless by-products such as CO_2 and H_2O , making it an environmentally friendly option.
3. Cost-Effective: Photocatalysts like TiO_2 are inexpensive, stable, and can be reused multiple times.
4. Low Energy Requirement: Photocatalysis can be driven by low-energy UV light, and even natural sunlight, reducing energy costs.

Photocatalysis represents a promising and sustainable approach for the degradation of organic pollutants in wastewater. By leveraging light energy to activate semiconductor photocatalysts, this technology offers an efficient and eco-friendly solution for water purification. Ongoing research and development aim to enhance the performance and scalability of photocatalytic systems, paving the way for their widespread application in addressing water pollution challenges.

Photocatalytic oxidation, a prominent subset of AOPs, has garnered significant interest due to its unique attributes. Utilizing semiconductor photocatalysts like TiO_2 under UV light, this process stands out by requiring low-energy UV-A light and reusable catalysts, eliminating the need for additional strong oxidants. Furthermore, photocatalysis is capable of harnessing solar energy, with approximately 3% of the solar spectrum reaching Earth being in the UV-A range. The primary benefits of photocatalysis over conventional methods include:

1. **Broad Spectrum Mineralization:** Almost all organic pollutants, including those resistant to $\text{OH}^\bullet$ such as CCl_4 , can be fully mineralized.
2. **Eco-friendly Process:** This green technology results in benign degradation products such as CO_2 , H_2O , and mineral acids.
3. **Oxygen Utilization:** Atmospheric oxygen acts as the oxidant, negating the need for external oxidants.
4. **Cost-Effectiveness and Stability:** Photocatalysts are inexpensive, non-toxic, stable, inert both biologically and chemically, insoluble under most conditions, and reusable.
5. **Energy Efficiency:** Low-energy UV light is used for photocatalyst activation, and solar light can also be utilized.
6. **Economic Competitiveness:** The process is economically comparable to the activated carbon adsorption method for medium to large capacities.

Photocatalytic reactions are initiated by the irradiation of semiconductor particles, such as TiO_2 , by UV light with energy exceeding the semiconductor's band gap energy. This irradiation generates e^-/h^+ pairs within the semiconductor. These pairs then participate in redox reactions, oxidizing or reducing adsorbed organic and inorganic compounds. [9]

The electronic structure of semiconductors, characterized by a filled valence band and an empty conduction band, makes them ideal photocatalysts. Upon absorption of a photon with sufficient energy, an electron is excited from the valence band to the conduction band, leaving behind a positively charged hole in the VB.

This process can be mathematically described by the equation:

$$\lambda_{bg}(nm) = 1240/E_{bg} (eV) \quad (2.1)$$

While many semiconductors, including TiO₂, ZnO, ZnS, WO₃, and CdS, have been explored for photocatalytic applications, TiO₂ remains the most widely utilized due to its suitable band gap and stability. However, TiO₂'s activation is limited to UV light, prompting efforts to develop photocatalysts that operate under visible light. Methods to achieve visible-light activation include metal ion implantation, metal doping, valence band modification through the addition of appropriate atoms, and the formation of solid solutions. Additionally, photosensitization using suitable dyes can extend the absorption range of photocatalysts to the visible spectrum. [9]

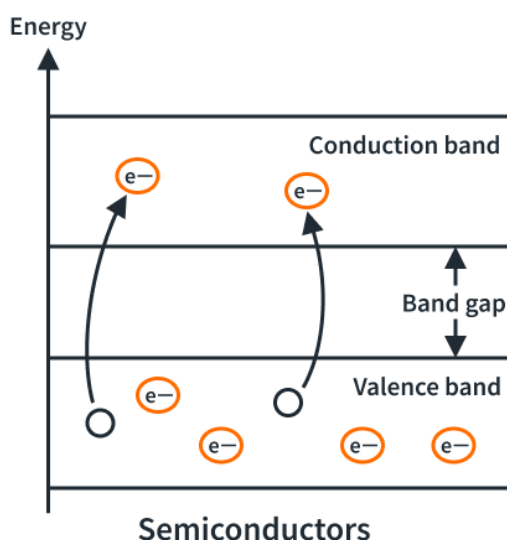


Figure 2.4: Band gap energy diagram of semiconductors.

ZnO is another widely studied semiconductor for photocatalysis. It has a similar band gap energy to TiO₂ (approximately 3.2 eV), making it suitable for UV light absorption. However, ZnO is less stable in aqueous environments due to its tendency to dissolve and form Zn(OH)₂ on its surface, which can deactivate the catalyst over time.

ZnS has a larger band gap energy (around 3.6 eV), which makes it efficient under UV light. Despite its potential, ZnS suffers from low photocatalytic efficiency and photo-instability, limiting its practical application in wastewater treatment.

WO₃ is a visible-light-active semiconductor with a band gap energy of approximately 2.8 eV. However, it is generally less photocatalytically active compared to TiO₂ and suffers from lower stability and efficiency under typical photocatalytic conditions.

CdS is a semiconductor with a smaller band gap (around 2.4 eV), making it responsive to visible light. Nevertheless, its use is limited due to severe photo-corrosion and the toxicity of cadmium, which raises environmental and health concerns.

Fe₂O₃, or hematite, has a band gap of about 2.2 eV, enabling it to absorb visible light. Despite this, its photocatalytic activity is much lower than TiO₂, and it often suffers from poor charge carrier mobility and rapid recombination of e⁻/h⁺ pairs [9].

Despite the progress made with traditional semiconductor photocatalysts, there is a pressing need for next-generation materials that can address the limitations of existing photocatalysts. Current challenges include the requirement for UV light activation, limited efficiency under visible light, stability issues, and potential environmental and health risks associated with some materials. Next-generation photocatalysts should aim to:

1. Enhance Visible Light Absorption: Develop materials with narrower band gaps that can efficiently utilize a larger portion of the solar spectrum, especially visible light.
2. Improve Stability: Design photocatalysts that maintain high activity and stability under operational conditions, minimizing issues like photo-corrosion and dissolution.
3. Increase Efficiency: Optimize charge carrier dynamics to reduce recombination rates and enhance the separation and transfer of photo-generated e⁻/h⁺ pairs.
4. Environmental and Health Safety: Focus on non-toxic, environmentally benign materials to avoid potential health risks and environmental contamination.
5. Cost-Effectiveness: Ensure that new materials are economically viable for large-scale production and application in water treatment

Advancements in material science, nanotechnology, and molecular engineering hold promise for developing these next-generation photocatalysts, offering more efficient, stable, and sustainable solutions for wastewater treatment and beyond.

Table 2.2: Band gap energy of semiconductor photocatalysts[9].

Semiconductor	Band gap (eV)	Wavelength (nm)	Energy (kcal/mol)
SnO ₂	3.8	326	87.7
ZnS	3.6	344	83.1
ZnO	3.2	388	73.8
WO ₃	3.2	388	73.8
TiO ₂	3.2	388	73.8
SrTiO ₃	3.2	388	73.8
SiC	3.0	413	69.2
CdS	2.5	496	57.5
Fe ₂ O ₃	2.3	539	53.1
GaP	2.25	551	51.9
CdSe	1.7	730	39.2

2.3. Metal-Organic Frameworks

MOFs are porous and crystalline structures composed of inorganic metal clusters connected by organic ligands. These materials are notable for their extensive surface area, customizable pore sizes, and structural versatility, which render them highly suitable for diverse applications such as gas storage, separation processes, catalysis, and drug delivery.[10]

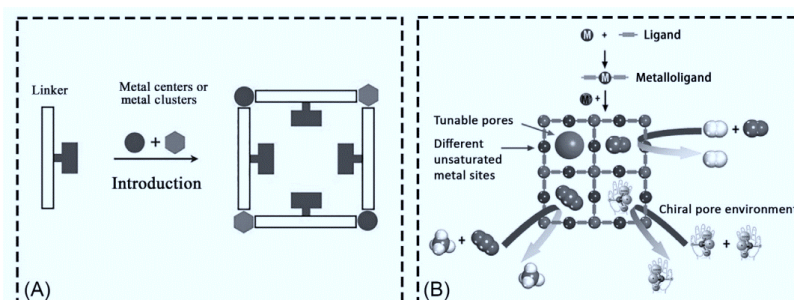


Figure 2.5: Schematic of metal-organic framework [10].

This phenomenon is a result of the interaction between the metal centers in the framework and the conjugated π -systems of the organic ligands. The metal centers function as active sites for catalytic processes, while the organic ligands serve as light-absorbing antennas that enable the transfer of light energy to trigger chemical changes.

A significant benefit of MOFs in photocatalysis is their high capacity to effectively absorb light energy across a wide range of wavelengths, encompassing visible light. This capacity is essential for solar-powered photocatalytic activities, such as the splitting of water to produce H_2 , the reduction of CO_2 , and the breakdown of organic contaminants. By carefully choosing metal nodes and organic ligands, researchers can enhance the photocatalytic performance of CPs. This is done by altering the material's band gap structure to increase light absorption and catalytic efficiency. Furthermore, the notable characteristics of CPs, such as their substantial surface area and enduring porosity, facilitate the effective adsorption of reactants. This, in turn, boosts their catalytic activity and stability across a range of reaction circumstances. Their inherent capacity to adapt their structure enables the attachment of various ligands and metal centers, hence broadening their potential use in tailored photocatalytic systems. MOFs are a state-of-the-art type of materials in photocatalysis. They utilize their distinct structural and electrical characteristics to efficiently transform light energy into chemical energy. Further exploration and improvement in the design and synthesis of MOFs are anticipated to propel progress in sustainable energy technologies and environmental remediation solutions on a global scale [10].

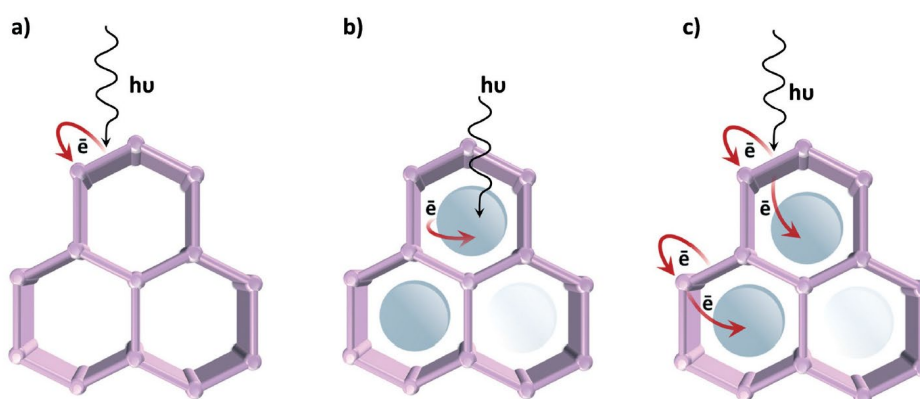


Figure 2.6: Approaches for promoting photocatalytic activity in MOFs [11].

MOF photocatalysts often function using either UV or visible light. Photocatalytic species, such as semiconductors, absorb light energy and produce e^-/h^+ pairs. The e^- and h^+ go towards the surface of the MOF. Electrons and holes at the MOF surface engage in redox reactions with H_2O or adsorbed pollutants. When water is present, e^- have the ability to decrease the amount of O_2 and create $O_2^{\bullet-}$. At the same time, h^+ can increase the amount of H_2O and generate $\bullet OH$. Reactive oxidant species, such as $O_2^{\bullet-}$ and $\bullet OH$, react with pollutants, leading to their oxidation or breakdown into innocuous substances including organic colors, medications, pesticides, heavy metals, and microbes [11,12].

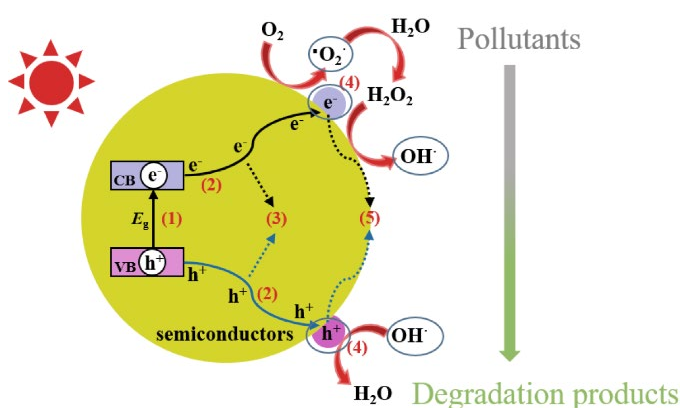


Figure 2.7: Photocatalytic mechanisms in CPs [12].

The presence of pollutants in water solutions undergoes degradation as long as the MOF photocatalyst is exposed to light, resulting in the ongoing generation of reactive oxidant species. MIL-101(Cr), composed of chromium ions and terephthalic acid ligands, is an enduring MOF employed for the purpose of water filtration. MIL-101(Cr) is highly successful in removing heavy metals, organic dyes, and medicines from water due to its large surface area and ability to adjust pore size. ZIF-8, UiO-66(Zr), MIL-125(Ti), MIL-101, MIL-53, and MIL-88B are well-researched MOFs that employ light to transfer photogenerated electrons for the purpose of water treatment by photocatalysis [13].

For instance, Laurier et al. conducted a study to examine the photocatalytic efficiency of several Fe-MOFs (MIL-88B, MIL-100, and MIL-101) in breaking down RhB using visible light at a wavelength of 550 nm. Recent progress in the synthesis and modification of MOFs has resulted in the identification of multiple MOFs in scientific publications that have shown promise in photocatalytic water treatment. These studies have specifically investigated the efficacy of these MOFs in removing different types

of pollutants, such as dyes, heavy metals, priority pollutants, and emerging contaminants [13]. Due to the outcome of the fundamental properties of MOFs that make them highly suitable for photocatalytic applications are as follows:

High Surface Area: MOFs possess extremely high surface areas, which provide more active sites for catalytic reactions to occur.

Adaptable Topologies: The structural design of MOFs can be tailored, which means that their pore sizes and shapes can be modified to fit specific needs.

Functionalization Ability: MOFs can be functionalized with different ligands and metal centers, allowing for a range of catalytic activities depending on the application requirements.

Tunable Pore Channels: The pore structure in MOFs can be precisely controlled, which is critical for the diffusion and interaction of reactant molecules within the framework.

High Surface-to-Volume Ratios: The extensive surface area relative to their volume enhances MOF's interactions with light and reactant molecules.

Rich Compositions: MOFs can offer a variety of compositions due to the different combinations of metal ions and organic linkers, influencing their photocatalytic properties and efficiency [13].

Overall, MOFs show great potential as photocatalysts for the degradation of organic dyes in the process of treating wastewater. Comprehending the mechanisms and factors that affect the breakdown of dyes through exposure to light is essential in order to create effective and specific photocatalysts for the purpose of treating water.

2.3.1. Ligands Used in the Synthesis of MOFs

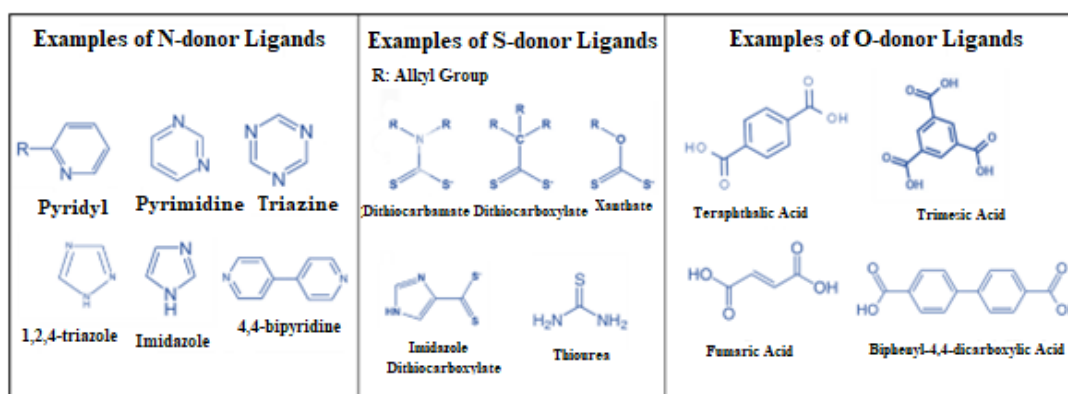


Figure 2.8: Ligands used in the synthesis of MOFs [14].

The choice of ligands employed in the synthesis of MOFs is critical as it profoundly impacts the structural and functional characteristics of the resultant molecules. Ligands in MOFs are frequently chosen to be organic molecules. Ligands containing many donor atoms, such as N, O, and S, are essential for the repeating structure of the polymer [14]. Py is a typical N-donor ligand that can coordinate to metal ions due to the presence of a lone pair of electrons on N. Another noteworthy ligand is 2,2'-bpy, which is distinguished by its two pyridine rings that have the ability to attach to metal centers, resulting in the formation of stable complexes. 1,10-Phenanthroline (phen) is a bidentate ligand that contains N atoms capable of coordinating with metals, leading to the formation of luminous complexes. OAc is an O-donor ligand that functions as a monodentate ligand by binding through a single O atom. Ethylene glycol (EG) acts as a ligand that forms coordination bonds with metal ions by utilizing two O atoms. Moreover, citrate, which is a ligand with three binding sites, offers three O atoms that can coordinate with metal centers. This is a frequent feature observed in metal complexes found in biological systems.

Thiocyanate (SCN) acts as a monodentate ligand in the case of S-donor ligands, binding to metal ions through sulfur. Thiols, which are organic molecules containing sulfur, function as monodentate ligands by binding through the sulfur atom. Dithiocarbamates are a type of ligand that have two sulfur atoms that coordinate with metal ions. They are commonly employed in metal extraction and coordination chemistry [15].

The ligands exhibit varying electron-donating capabilities towards metal ions, which in turn affect the stability and characteristics of the resulting CPs or complexes.

2.3.2. Synthesis Methods of MOFs

MOFs are structured substances composed of metal ions or clusters that are coordinated with organic ligands. These frameworks can be created using many methods, including reflux synthesis, solvothermal synthesis, hydrothermal synthesis, microwave-assisted synthesis, and mechanochemical synthesis.

The choice of synthesis process employed to fabricate a MOF can exert a substantial impact on its characteristics, including the dimensions and structure of its crystals, which subsequently influence its efficacy in diverse applications.

Explores different synthesis techniques and their influence on the properties of MOFs. Varying synthesis methods can have a substantial impact on the size, shape, and production rate of MOFs. Each technique yields distinct particle sizes [16].

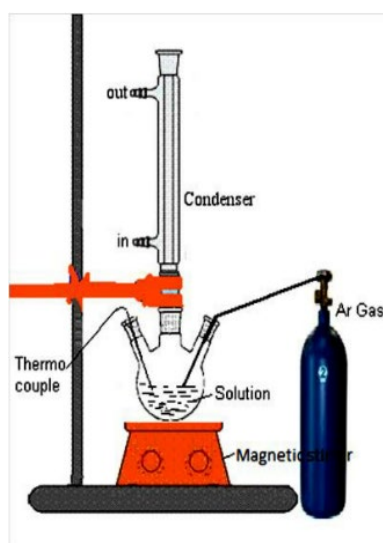


Figure 2.9: Schematic diagram of reflux method [17].

The reflux method is a widely utilized methodology in the synthesis of MOFs that improves reaction kinetics and increases product yield. The process entails introducing the reaction mixture into an appropriate solvent within a reflux unit. This device usually comprises a flask with a curved bottom that is fitted with a vertical condenser.

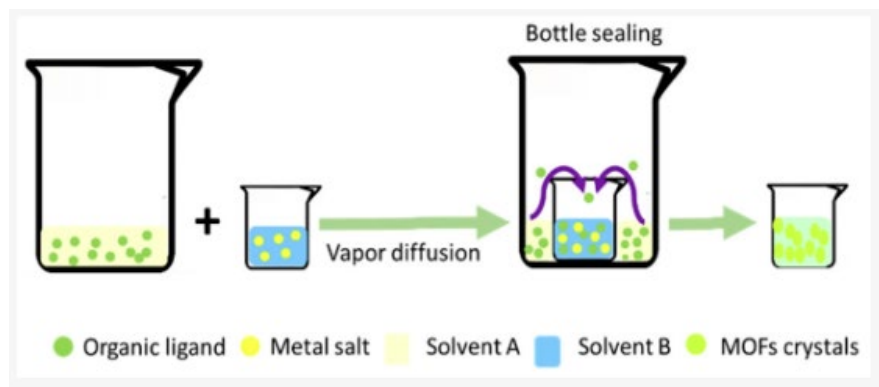


Figure 2.10: Schematic diagram by the gas phase diffusion method [18].

This procedure can be approached in two ways, depending on the gradual transportation and interaction of different species. The initial method entails solvent-liquid diffusion. At first, two layers with distinct densities are formed, with a third layer of solvent separating them. One of these layers contains the solvent that causes precipitation, while the other layer surrounds the product in a separate solvent. At the boundary between these layers, the solvent that causes precipitation slowly spreads into the separating layer, which encourages the formation of crystals. The second method employs physical barriers to facilitate the slow dispersion of reactants. This technique commonly utilizes two vials of varying diameters. In addition, gels can serve as mediums for the processes of crystallization and diffusion on certain occasions. They have the ability to efficiently decrease the speed at which particles spread and hinder the formation of large amounts of solid material. The diffusion approach facilitates the generation of singular crystals, which are highly valuable for the purpose of XRD investigation. This method offers significant benefits in comparison to acquiring non-crystalline or poly-crystalline items, particularly when those items are insoluble [18].

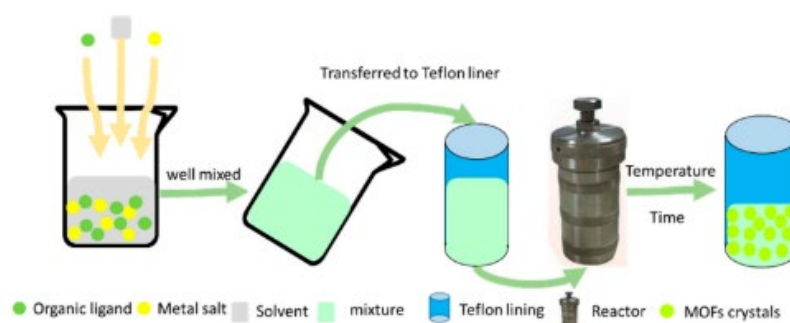


Figure 2.11: Schematic diagram of hydro/solvothermal synthesis [18].

Hydro/Solvothermal Synthesis refers to a method of chemical synthesis that involves using a solvent at high temperature and pressure conditions. Hydrothermal synthesis involves using water at high temperatures and pressures to create single crystals by taking advantage of the minerals's solubility under these specific conditions. Solvothermal synthesis involves the utilization of several solvents under circumstances that are either near critical or supercritical. Solvothermal synthesis is a more encompassing term that encompasses hydrothermal synthesis. They are frequently used interchangeably inside the framework of MOFs. Hydrothermal and solvothermal methods are commonly employed for the synthesis of MOFs because of their capacity to manipulate crystal size, shape, and structure [18].

Electrochemical synthesis is a technique that use electrical current to catalyze chemical processes. During this process, chemical reactions take place at the boundary between an electrode and an electrolyte, resulting in the direct conversion of electrical energy into chemical energy. By manipulating the applied voltage or current, certain reactions can be facilitated, resulting in the creation of desired compounds.

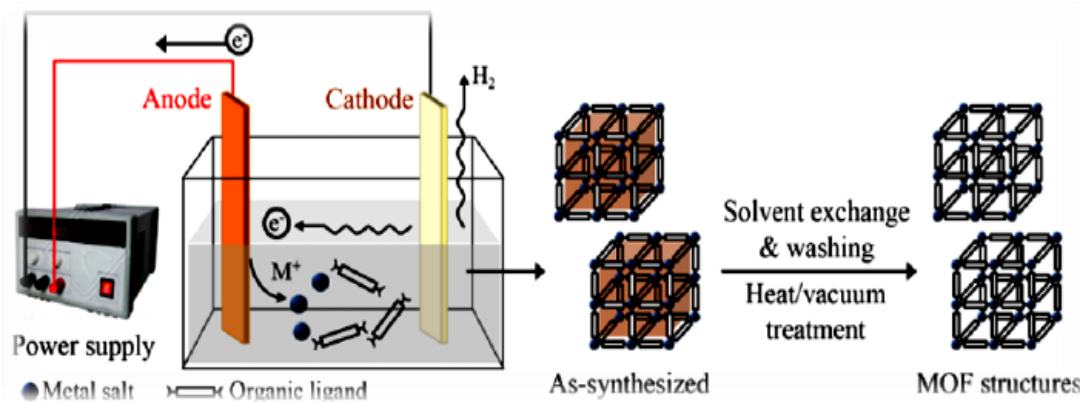


Figure 2.12: Schematic diagram of electrochemical synthesis [18].

This technique has benefits such as exceptional selectivity, precise control, and the capability to function at standard temperature and pressure. Consequently, it serves as a potent instrument in many domains, including organic and inorganic synthesis, material research, and energy storage [18].

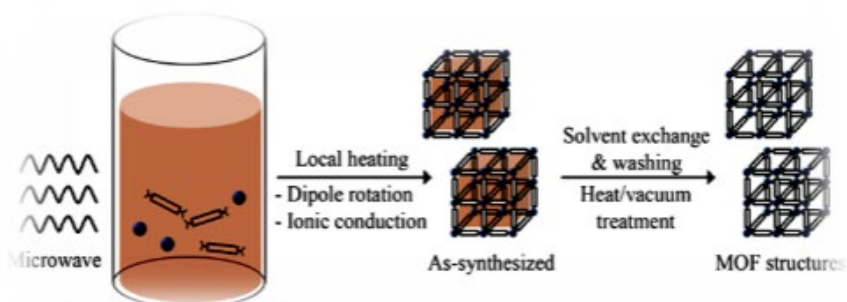


Figure 2.13: Schematic diagram of microwave synthesis [18].

Microwave synthesis is a contemporary method used to efficiently create MOFs. This process utilizes microwave irradiation to quickly and evenly heat a mixture of metal salts, organic linkers, and a solvent. This technique greatly expedites the reaction process, decreasing synthesis durations from hours or days to only minutes, and guarantees uniform heating, which enhances the uniform formation and development of superior MOF crystals. Microwaves enable efficient energy transfer, leading to increased solubility of reactants and accelerated reaction speeds. Microwave synthesis offers significant benefits due to its rapidity, energy efficiency, and capacity to accurately regulate the size and morphology of the resulting MOF crystals. Consequently, it is an optimal method for both research purposes and large-scale manufacturing of MOFs [18].

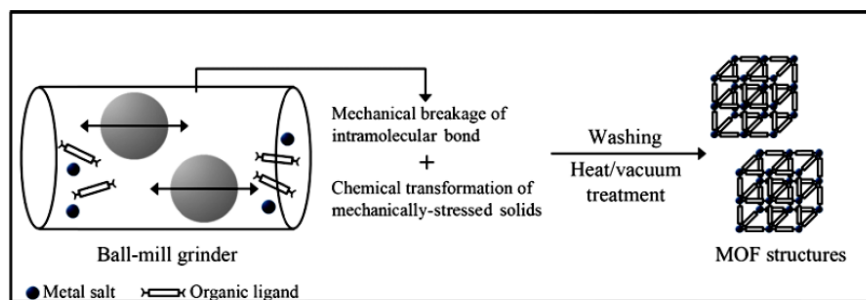


Figure 2.14: Schematic diagram of mechanochemical synthesis[18].

Mechanochemical synthesis employs mechanical force, such as grinding, milling, or crushing, to initiate chemical reactions. This approach, commonly referred to as "green chemistry," eliminates the need for solvents or high temperatures by utilizing mechanical force to disrupt chemical bonds and promote the creation of new ones. This procedure can be employed to produce a diverse array of substances, such as nanoparticles, metal alloys, and organic compounds. It frequently offers benefits such

as reduced reaction durations, increased product quantities, and the capacity to generate distinct materials with precise characteristics [18].

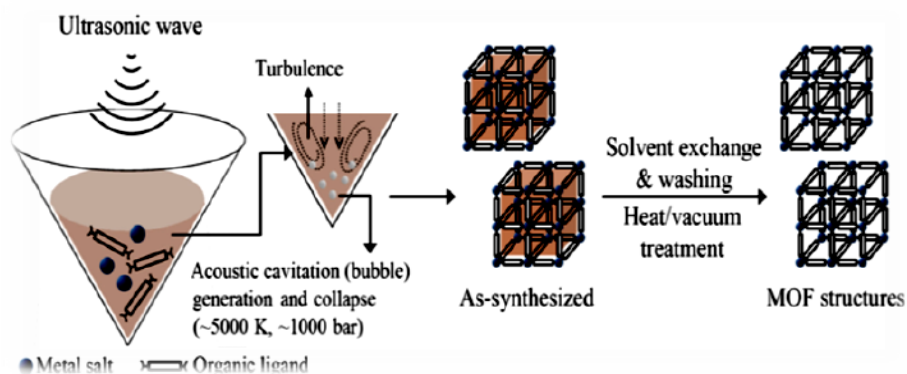


Figure 2.15: Schematic diagram of sonochemical synthesis [18].

This synthesis method relies on the principle of sonochemistry, which involves inducing a chemical reaction by exposing the substances to ultrasonic waves with frequencies ranging from 20 kHz (the highest frequency audible to humans) to 10 MHz. The formation of acoustic cavitation drives the process. Cavitation refers to the of creating, growing, and collapsing bubbles inside a liquid. Figure 2.15 shows an increase due to the collapse of cavitation. The process of synthesizing MOFs using solvothermal methods. The sonochemical method, often known as ultrasonic irradiation, is a technique used for many purposes in chemistry and materials science. This synthesis method relies on the principle of sonochemistry, which involves

inducing a chemical reaction through the application of ultrasonic waves with frequencies ranging from 20 kHz (the max limit of human hearing) to 10 MHz. Cavitation refers to the process of creating, growing, and collapsing bubbles inside a liquid. The cavitation breakdown leads to a rise in temperature (ranging from 5000 to 25,000 K) and pressure (1000 atm), together with high rates of heating/cooling and the occurrence of fast shock waves in the liquid around the bubble. Sonochemical synthesis leads to a gradual enhancement in the rate of the reaction, as well as an increased yield, improved energy efficiency, and enhanced particle synthesis. In addition, this product is environmentally benign, user-friendly, can be used at room temperature, and significantly reduces the time required for synthesis compared to other conventional synthesis methods [18].

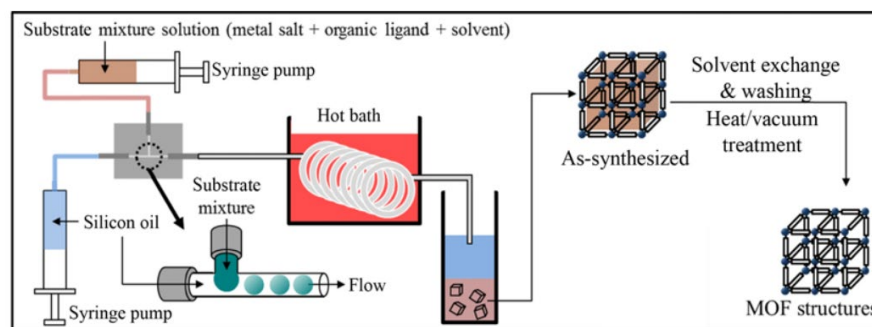


Figure 2.16: Schematic diagram of microfluidics synthesis[19].

The benefits of utilizing microfluidic synthesis in the creation of MOFs are highly varied. Primarily, this technology offers improved heat and mass transmission, hence expediting the reaction kinetics and leading to a more expedient and effective production process. Microfluidic systems provide highly accurate manipulation of reaction parameters, particularly variables such as temperature, pH, and concentration. The exact control guarantees that the end product's size and morphology are uniform, enabling the production of MOFs with the necessary qualities.

Moreover, microfluidic techniques facilitate the synthesis of compounds in extremely small quantities and with exceptional consistency by utilizing the uninterrupted movement of reaction mixtures and their arrangement in microreactors based on droplets. MOFs can be manufactured at many scales, ranging from small laboratory settings to large industrial operations consequently, microfluidic synthesis [18].

Post-synthesis modification methods surpass classical synthesis techniques for MOFs by using innovative approaches that strive to enhance the structural and functional characteristics of these materials. These techniques encompass chemical alterations or modifications performed subsequent to the initial synthesis of MOFs, hence augmenting their functionality [18,19].

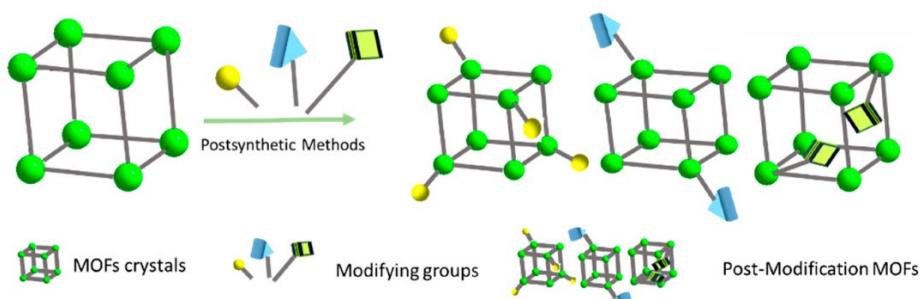


Figure 2.17: Schematic diagram of post-synthesis modification [18,19].

The primary characteristic of these strategies is to enhance the physical and chemical properties of MOFs by including novel functional groups or altering existing groups in the post-synthesis structure. By introducing distinct functional groups onto the surface of MOFs, it is possible to enhance gas storage capacity or confer catalytic activity. Moreover, MOFs can be adapted for utilization in biological applications, medication delivery systems, or sensor technologies.

Typically, these alterations are accomplished by a range of approaches including organic chemical processes, coordination chemistry, and surface chemistry. Post-modern synthesis techniques optimize the intricate architectures of MOFs, thereby unleashing the untapped potential of these materials for novel applications. Specifically, it has a crucial function in improving the efficiency of MOFs in various domains, including eco-friendly energy storage systems, catalysts, sensors, and medical applications.

Post-modern synthetic methods surpass the initial synthesis of MOFs, hence broadening the functioning and application domains of these materials [18,19].

2.4. Phosphazenes

Phosphazenes are a group of chemicals that consist of N and P atoms. Phosphazenes at their simplest form consist of a structure made up of alternating N and P atoms, usually arranged in a cyclic or polymeric chain. The compounds can be represented by the generic formula $(N=PR_2)_n$, where R is an organic substituent or a halogen, and 'n' can vary to indicate the number of P-N units in the molecule. [20] Phosphazenes can be manufactured via diverse chemical routes and possess flexible characteristics, making them suitable for applications in a range of applications, including flame retardants, elastomers, medicines, and materials with unique electrical and optical properties. Their chemistry is highly diverse because of the capacity to replace various groups on the P atoms, which can greatly modify their chemical and physical properties.

Phosphazenes are a group of chemicals distinguished by a P atom at the center that is bound to N atoms. These compounds possess a distinctive structure composed of P and N atoms arranged in an alternating pattern, resembling the backbone of rings. Phosphazenes exhibit diverse chemical formulas and structures, which are determined

by the specific arrangement and substitution of P and N atoms in a ring-like configuration. Phosphazenes possess a distinctive arrangement, which grants them a diverse array of characteristics and uses, such as in the fields of materials science, catalysis, and medicines [20].

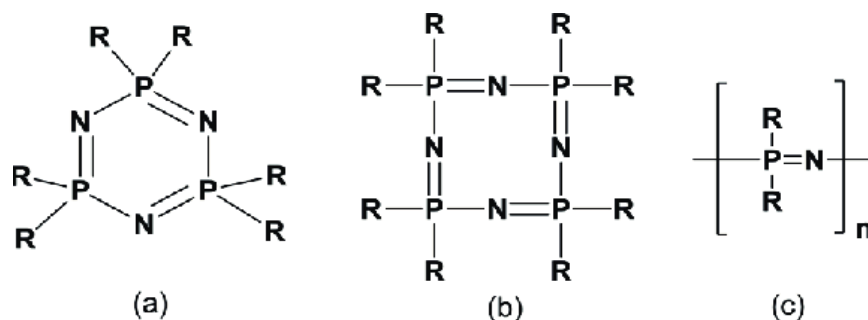


Figure 2.18: Phosphazene structures (a) trimer (b) tetramer (c) polyphosphazene.

Cyclotriphosphazenes have a lengthy historical background that can be traced back to the 19th century. The molecule was first synthesized in 1834 by Liebig and Wöhler by reacting NH_3 with PCl_5 . Although its structural identity was first unknown, its formula was discovered as NPCl_2 in 1844 by Gerhardt and Laurent. Later on, Gladstone and Holmes verified that the chemical formula of the substance was $(\text{NPCl}_2)_3$, indicating a cyclic structure. This idea was initially put up by Stokes. Progress in crystallography has provided additional clarity on the arrangement of molecules in this category of substances. In 1936, Meyer and colleagues did the initial X-ray structural analysis [20,21].

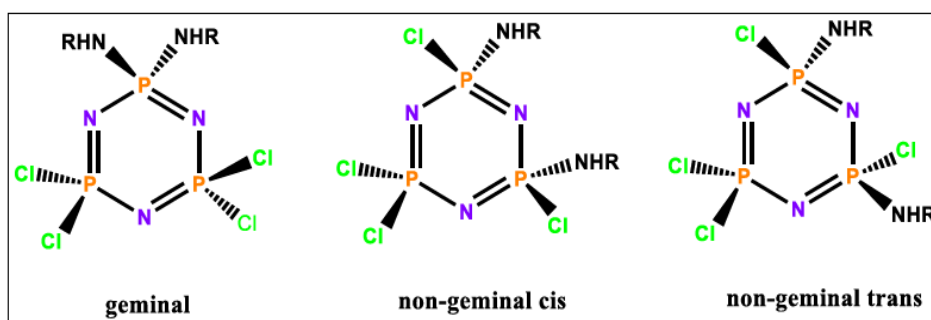


Figure 2.19: Schematic diagram of geminal, non-geminal cis, non-geminal trans structures of cyclotriphosphazene.

Cyclotriphosphazenes have the ability to perform nucleophilic displacement reactions because of the presence of reactive P-halogen linkages in their structures.

By chemically bonding diverse compound groups such as thiols, alcohols, amines, and phenolic compounds, it is possible to create several types of cyclotriphosphazene compounds, each with distinct characteristics [22]. For instance, if the chlorine atoms in the trimer compound are substituted with aryloxy groups, the resulting compounds exhibit resistance to combustion and hydrolysis. These compounds have the potential to be utilized in the manufacturing of composites that are resistant to high temperatures.

Cyclotriphosphazenes contain N atoms in the ring that possess a high degree of basicity and are capable of interacting with Lewis acids. In addition, enlarging the cyclotriphosphazene ring improves its flexibility, hence enhancing its effectiveness as a ligand. The coordination chemistry of N atoms within the cyclotriphosphazene ring is somewhat restricted due to their basicity. The cyclotriphosphazene can offer coordination sites by ligand substitution. The versatility of the cyclotriphosphazene ring is greatly enhanced by this characteristic. The P-Cl bonds can be easily replaced to bind ligands to the P atom, allowing for the coordination of suitable groups [23]. The presence of this property makes cyclotriphosphazene molecules essential for coordination chemistry.

Recently, cyclotriphosphazene molecules have been widely used as essential building blocks in research on supramolecular and materials science. However, research on cyclotriphosphazene-based CPs remains scarce, as indicated by the limited number of studies conducted [24,25]. The literature describes cyclotriphosphazene structures coordinated with a restricted set of metals, including lanthanides (Ln^{3+}), Cu(II), Zn(II),

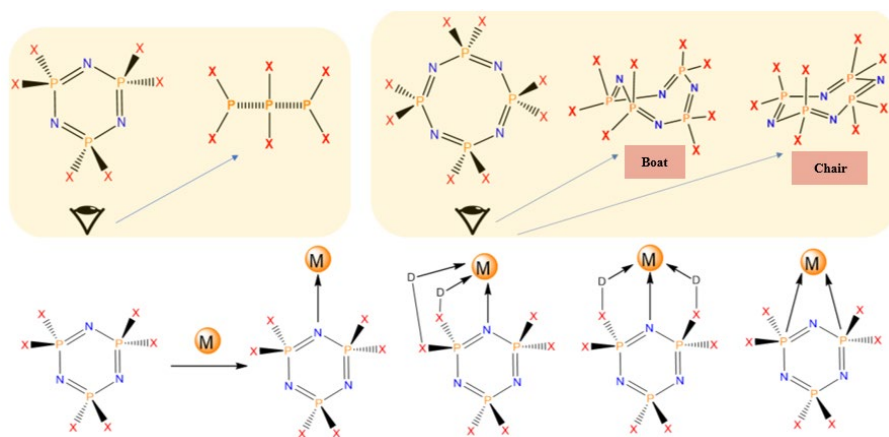


Figure 2.20: Representation of cyclic phosphazenes (above). Possible coordination states of a cyclotriphosphazene ring with a metal atom (below).

Pb(II), Co(II), Cd(II), and alkaline earth metals such as Mg(II), Ca(II), and Ba(II). Studies on cyclotriphosphazene CPs have investigated multiple aspects, including gas adsorption, hydrogen production, removal of VOCs, gas separation, 3D magnetic structures, and fluorescence sensors [26]. However, there is a notable lack of comprehensive research on utilizing photocatalysis for the decomposition of industrial waste and organic pigments present in wastewater [27,28].

The proposed study, which focuses on investigating the photocatalytic properties of phosphazene-based inorganic-organic hybrid CPs, aims to significantly enhance our global understanding in this field. The objective is to explore the potential applications of these compounds in environmental remediation and sustainable technology, with an emphasis on their importance for both academic research and industrial advancement.

2.4.1. Use of Phosphazenes as Ligands in MOFs

MOFs, composed of metal centers linked by organic ligands, have gained considerable attention for their wide range of applications, such as catalysis, gas storage, and sensing. Phosphazenes, characterized by their P-N backbone, are an intriguing class of ligands for MOFs due to their unique coordination modes and functions [29].

Phosphazenes have been extensively studied as ligands in CPs because they can bind to various metal centers via their P and N atoms. Their adaptability in coordination chemistry has led to applications ranging from nuclear fuel reprocessing to the development of photoluminescent devices. Specifically, significant research has been conducted on lanthanide phosphine oxide complexes to understand their structural properties and explore practical uses. Additionally, phosphazene-based ligands in luminous MOFs have shown potential as alternative phosphors for energy-efficient lighting and optoelectronic applications [30].

The exceptional stability of metal-N bonds in these coordination systems, coupled with their ability to incorporate additional coordinating molecules and ions, has expanded the utility of PCPs. These materials have demonstrated usefulness in applications such as gas sorption and homogeneous catalysis, further underscoring the breadth of their properties and the sustained interest in their advancement [31].

Phosphazenes have emerged as a promising option for designing unique materials with specific properties in the evolving field of CPs. Cyclotriphosphazenes have attracted considerable interest in the realm of CPs because of their distinctive structural features and adaptable coordination chemistry. The inclusion of cyclotriphosphazenes in CPs, namely as multicarboxylate ligands, has notable benefits, including exceptional thermal stability, luminous characteristics, and practical uses in catalysis and gas adsorption. This section explores the function of cyclotriphosphazenes in the advancement of CPs, emphasizing their importance in existing research and their potential for future investigations and practical uses [32].

Structural Characteristics of Cyclotriphosphazenes

Cyclotriphosphazenes are characterized by a cyclic framework consisting of alternating P and N atoms. This unique structure allows for the attachment of various functional groups, enhancing the ligand's coordination capabilities. When functionalized with carboxylate groups, cyclotriphosphazenes act as excellent multidentate ligands, forming robust and stable coordination networks with metal ions. The ability to introduce multiple carboxylate groups onto the cyclotriphosphazene ring further increases the versatility and complexity of the resulting CPs [33].

Importance in Coordination Polymers

1. **Chemical stability:** Cyclotriphosphazenes are known for their exceptional thermal and chemical stability, which is attributed to their unique cyclic framework consisting of alternating P and N atoms. This stability is further enhanced when functional groups, such as carboxylate groups, are introduced, making cyclotriphosphazenes ideal candidates for constructing robust CPs. The inherent stability of cyclotriphosphazenes ensures that the resulting CPs can withstand high temperatures and harsh chemical environments, which is crucial for various industrial and environmental applications [33].
2. **Thermal Stability and Structural Robustness:** Cyclotriphosphazene-based ligands contribute significantly to the thermal stability of CPs. Studies have demonstrated that CPs incorporating cyclotriphosphazenes exhibit high decomposition temperatures, often exceeding 300°C, making them suitable for applications that require thermal resilience. For example, the CPs GTU-1 and GTU-2, synthesized using a cyclotriphosphazene-based ligand, showed

thermal stability up to 330°C, with GTU-2 exhibiting superior catalytic performance in dye degradation applications. [34]

luminescent Properties: The luminescent properties of cyclotriphosphazene-based CPs are of particular interest for applications in sensing and optoelectronics. Lanthanide MOFs (Ln-MOFs) utilizing cyclotriphosphazene ligands have been reported to exhibit strong luminescence, making them effective in detecting VOCs and other analytes. For instance, the Ln-MOFs synthesized by Shuang Yu demonstrated selective sensing of VOCs, with tunable emission colors achieved by incorporating different dyes into the framework. [35]

3. **Catalytic Activity:** Cyclotriphosphazene-based CPs have shown promising catalytic properties, particularly in the degradation of environmental pollutants and the synthesis of organic compounds. The study by Velusamy Jeevananthan highlights the development of an Indium(III)-based MOF using a cyclotriphosphazene ligand, which exhibited high catalytic efficiency and reusability in cyclization reactions to produce bioactive compounds. This research underscores the potential of cyclotriphosphazene-based catalysts in green chemistry and sustainable synthesis. [36]
4. **Versatile Coordination Chemistry:** The versatile coordination chemistry of cyclotriphosphazenes allows for the formation of complex and stable coordination networks. The multiple coordination sites available on cyclotriphosphazene ligands enable the construction of 3D frameworks with diverse topologies. This versatility is exemplified in the study by Velusamy Jeevananthan, where an Indium (III)-based MOF was synthesized using HCPCP ligands, resulting in a stable and reusable catalytic system. [36]
5. **Gas Adsorption and Separation:** CPs that contain cyclotriphosphazenes have a porous structure, which makes them well-suited for applications involving the adsorption and separation of gases. The holmium-based Ln-MOF shows promise in natural gas purification due to its ability to selectively adsorb C₂ hydrocarbons over CH₄. The versatile coordination environment offered by cyclotriphosphazene ligands improves the specificity and capability of the framework for particular gases. [37]

Objectives and Scope of the Thesis

The primary goal of this thesis is to develop and evaluate new carboxylate-based CPs for their effectiveness in removing dyes from wastewater through photocatalysis. This research aims to address the significant environmental issue of water pollution by exploring advanced materials and methods. Specifically, the thesis focuses on the synthesis of novel CPs using innovative cyclotriphosphazene/N-donor mixed ligands, and the development and characterization of four particular cyclotriphosphazene based CPs (**PCP-3**, **PCP-4**, **PCP-5**, **PCP-6**). These PCPs are analyzed using techniques such as XRD, TGA, FTIR, and SEM to thoroughly understand their structures.

- The photocatalytic performance of these PCPs is evaluated by testing their effectiveness in degrading common dyes like MB, MO, RhB, and RO16.
- The research delves into the mechanisms involved in the dye degradation process to provide a comprehensive understanding of the PCPs's capabilities.

Additionally, the thesis investigates the luminescence and optical properties of the MOFs, exploring their potential applications in sensors and optical devices. The study also assesses the reusability and stability of the MOFs, determining their durability in multiple cycles of dye degradation and evaluating their thermal and structural robustness.

Structure of the Thesis

This thesis is organized into several chapters, each contributing to a comprehensive understanding of the research conducted.

The Introduction chapter provides an overview of water pollution, emphasizing the importance of removing dyes from wastewater. It introduces the concept of photocatalysis and highlights the potential of CPs in environmental applications.

The Water Treatment Techniques chapter reviews various methods for dye removal, including physical, biological, and chemical processes, with a particular focus on advanced oxidation processes and the role of photocatalysts.

The Materials and Methods chapter describes the chemicals and equipment used in the research, detailing the synthesis procedures for the PCPs and explaining the methods employed in photocatalytic testing.

The Experimental Results chapter presents the findings from the synthesis and structural characterizations of the PCPs, followed by an analysis of their photocatalytic performance and optical properties.

The Discussion chapter interprets these results, providing insights into the effectiveness and potential applications of the PCPs in real-world scenarios.

Finally, the Conclusions chapter summarizes the key findings of the research, discussing the implications for future studies and the potential for these PCPs to be used in environmental remediation.

3. LITERATURE REVIEW

The use of cyclotriphosphazenes in CPs has been well-documented in the literature, with numerous studies highlighting their multifunctional properties and potential applications. Table 3.1. provides a comprehensive overview of CPs built using cyclotriphosphazene-functionalized multicarboxylates, highlighting their diverse properties and applications in luminescence, catalysis, and gas adsorption. Notable examples include:

Luminescent Properties: CPs such as lanthanide complexes exhibiting strong luminescence, ratiometric fluorescence detection capabilities.

- **Catalytic Activity:** Cadmium (II) CPs demonstrating catalytic efficiency in dye degradation.
- **Gas Separation:** Holmium-based Ln-MOFs highlighting selective gas adsorption properties.

Cyclotriphosphazenes are essential in developing advanced CPs due to their structural robustness, luminescence, catalytic activity, and gas adsorption capabilities. Their unique coordination chemistry and multifunctional properties make them invaluable for applications such as environmental remediation, sensing, and catalysis. The stability of cyclotriphosphazenes is crucial, as they can withstand elevated temperatures and resist chemical degradation, ensuring the resulting materials are robust and dependable. Their versatile coordination chemistry allows for complex frameworks with enhanced catalytic and adsorptive properties. Ongoing research continues to uncover new possibilities, significantly advancing coordination chemistry and material science. As this research progresses, cyclotriphosphazene-based CPs will play a key role in developing new materials for industrial, environmental, and catalytic applications.

Table 3.1: CPs built up by cyclotriphosphazene functionalized multicarboxylates in the literature.

Ligand	Metal ion	CSD Ref. Code	Dimensionality	Properties	Ref.
L1	Ho(III)	ORAGOF (ZJNU-61)	3D	Selective gas adsorption	[37]
L1	Cd(II)	LENGAO	3D	Luminescent properties	[38]
L1	Cd(II)	LENGES	3D		
L1	Eu(III)	ZINJUD	2D	Luminescent properties	[39]
L1	Eu(III)	ZINKAK	2D		
L4	Eu(III)	ZINKEO	1D		
L1	Zn(II)	WITKIV	3D	Luminescent properties	[40]
L1	Cu(II)	AHOLAM (ZJNU-60)	2D	Gas separation	[41]
L1	Mg(II)	ORUKET	3D	Luminescent properties	[42]
	Ca(II)	ORUKIX	3D		
	Ba(II)	ORUKOD	3D		
L3	Cd(II)	HEHZAY	3D	Luminescent properties	[43]
L2-OMe	Pb(II)	KEKBIG (ZJNU-62)	3D	Gas separation	[44]
L2-OMe L2-Cl L2-Br L2-Me	Ho(III)	UDIWOW (ZJNU-63)	3D	Gas adsorption properties	[45]
	Ho(III)	UDIWEM (ZJNU-64)			
	Ho(III)	UDIWUC (ZJNU-65)			
	Ho(III)	UDIWIQ (ZJNU-66)			
L1	Cd(II)	VEYSAW	3D	Luminescent properties	[46]
L4	Cd(II)	VEYSEA	2D		
L1	Eu(III),	XIFHEC	3D	Luminescent properties	[47]
L1	Tb(III)	XIFHIG	3D		
L1	Ni(II)	KIZCUU (Ni-MOF)	3D	Supercapacitor electrode	[48]
L1	Eu(III),	FOJROO (Eu-L1)	3D	Ratiometric fluorescence detection	[49]
L1	Tb(III)	FOJRUU (Tb-Eu1)	3D		
L1	Mn(II)	ZOHJOY	3D	Solvochromic Behavior	[50]
L1	Mn(II)	ZOHJUE	3D		
L5	Cd (II)	GEKPEZ	3D	Catalytic Activity	[51]
	Cd (II)	GIKTED	3D		
H4L1	Cd(II)	PCP-1	1D	Photocatalytic activity	[52]
H4L2	Cd(II)	PCP-2	1D	Photocatalytic activity	[52]

The study conducted by Velusamy Jeevananthan in 2024 centers around the creation of an environmentally friendly heterogeneous catalytic system. The research team created a new MOF called SRMIST-1 by combining Indium(III) with HCPCP ligands. The objective was to develop a catalyst that exhibits excellent thermal and chemical durability, strong catalytic activity, and remarkable reusability, in response to the increasing need for sustainable approaches in the production of intricate organic molecules. SRMIST-1 was produced through the reaction of indium(III) nitrate hydrate and HCPCP ligands, resulting in the formation of a 3D CPs with a pentagonal bipyramidal geometry of indium(III) cations. The characterisation methods utilized encompassed SCXRD, PXRD, FT-IR, NMR, elemental analysis, and TGA. These procedures unveiled the stability of the MOF up to 405°C and its resilience against different solvents. The catalyst's efficacy was evaluated in the cyclization reactions of 2-aminobenzamide and 2-aminobenzenesulphonamide with different aldehydes to get 2,3-dihydroquinazolin-4(1H)-ones (DHQs) and 3,4-dihydro-2H-1,2,4-benzothiadiazine-1,1-dioxides (DHBDs). SRMIST-1 demonstrated exceptional catalytic efficacy under gentle circumstances, utilizing a minimal amount of catalyst (1–5 mol %), employing EtOH as an environmentally friendly solvent, and resulting in products of high quality and yield. The catalyst's reusability was proven by its capacity to function efficiently for a minimum of five cycles without any substantial decrease in activity. This was additionally reinforced by the maintenance of its crystalline structure, as verified by PXRD, and its uniform surface appearance detected through SEM research. The hypothesized mechanism entails the creation of an active carbonyl intermediate, which is assisted by the Lewis acid catalyst SRMIST-1. The intermediate molecule experiences intramolecular nucleophilic assault, resulting in the creation of a hydroxy intermediate. This hydroxy intermediate then removes water to generate a Schiff base. The required DHQs are obtained through the subsequent 6-iminolendo-trig cyclization and a [1,5-H] shift. The catalyst is regenerated to be used in further cycles. An analogous mechanism was suggested for the synthesis of DHBDs. The paper emphasizes the notable benefits of SRMIST-1, such as its capacity to work with a wide range of functional groups, its requirement for a small amount of catalyst, its moderate reaction conditions, its simple workup methods, and its economic feasibility due to the catalyst's sustainability and ability to

be reused. The results suggest that SRMIST-1 is a highly responsive and recyclable environmentally friendly catalyst, making it well-suited for many uses in the field of medicinal chemistry. This study makes a valuable contribution to the field by introducing a sustainable and efficient approach to producing bioactive aza-heterocycles. It also demonstrates the promise of MOFs in the fields of green chemistry and heterogeneous catalysis. The creation of SRMIST-1 highlights the significance of developing environmentally friendly catalytic systems that adhere to the principles of green chemistry, fostering sustainability and minimizing the environmental consequences of chemical synthesis [36].

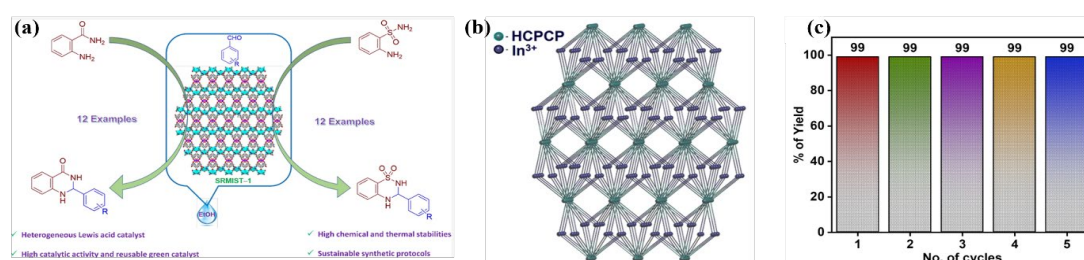


Figure 3.1: Studies of CP In-MOF [36].

A study conducted by A. O. Erkovan examines the process of creating two cadmium(II) CPs, GTU-1 and GTU-2. The study focuses on analyzing the structure of these polymers and evaluating their effectiveness as catalysts. The findings of this study may be found in the article titled. [30] The CPs were created using a unique hexapod-shaped molecular building block, hexakis(methyl-2-(4-phenoxyphenyl)acetatebenzene) cyclotriphosphazene (H_6L_1), by solvothermal reactions in DMF with HNO_3 as a modulator. GTU-1 has a structure composed of 3D pillared-layered CPs. These CPs comprise a 2D inorganic building unit (IBU) based on Cd-carboxylate ($Cd(COO)_n$). On the other hand, GTU-2 is formed by connecting 1D IBUs using deprotonated H_6L_1 and 4,4-bpy as an additional linker. GTU-1 and GTU-2 were extensively studied using FT-IR, TGA, SEM, PXRD, and SCXRD. The main objective of the work was to assess the catalytic efficiency of these CPs in breaking down dyes, namely RhB, MB, and AR-17, in water-based solutions. GTU-2 demonstrated higher catalytic efficiency than GTU-1 in eliminating these dyes. The degradation mechanism involved the activation of persulfate (PMS) by the CPs. The versatile cyclotriphosphazene-derived ligand (H_6L_1) performed a pivotal role in facilitating diverse binding modalities and modulating different molecular

arrangements, hence augmenting the catalytic efficiency. The catalytic activity was evaluated by measuring the changes in dye concentration using UV-Vis spectrophotometry. The hypothesized process for dye degradation encompasses both radical and non-radical routes. The production of sulfate radicals ($\text{SO}_4^{\cdot-}$) by the interaction of PMS with the metal centers of the CPs has been recognized as a crucial element in the degradation process. The availability of additional active Lewis acid sites in GTU-2's structure, facilitated by the 4,4-bpy auxiliary linker, resulted in improved catalytic performance. TGA indicated that both GTU-1 and GTU-2 exhibit excellent thermal stability, with breakdown temperatures surpassing 330°C. This characteristic renders them well-suited for practical use in wastewater treatment. The catalysts's reusability was CPs maintained their structural integrity and catalytic performance across repeated usage. The research findings indicate that the synthesized Cd(II) CPs, specifically GTU-2, have proven to be efficient catalysts for breaking down different dyes in water. This demonstrates their potential use in environmental remediation. The results underscore the significance of creating adaptable, versatile ligands to improve the efficiency of CPs in catalytic reactions. This study serves as a significant point of reference for future investigations into the catalytic uses of MOFs and CPs in the removal of dyes and other environmental applications. The study contributes to the ongoing efforts in developing sustainable and effective solutions for wastewater treatment and environmental protection by emphasizing the importance of creative ligand design and the effectiveness of GTU-2 in dye degradation [51].

The study conducted by Shuang centers around the creation, production, and analysis of a range of luminescent lanthanide MOFs (Ln-MOFs). These frameworks were synthesized using a versatile functionalized cyclotriphosphazene hexacarboxylic acid ligand known as hexakis(4-carboxylatephenoxy) cyclotriphosphazene (HCPCP). The work investigates the application of these Ln-MOFs in the specific detection of VOCs and the development of dye-encapsulated composites with adjustable emission colors. The synthesized Ln-MOFs consist of lanthanum (La), praseodymium (Pr), neodymium (Nd), gadolinium (Gd), and holmium (Ho). These compounds form 3D structures with $[\text{Ln}_3(\text{COO})_{10}]$ secondary building units coupled through HCPCP, resulting in rectangular channels along the c-direction. The structural investigation indicated that these compounds possess significant porosity, a substantial specific surface area, and

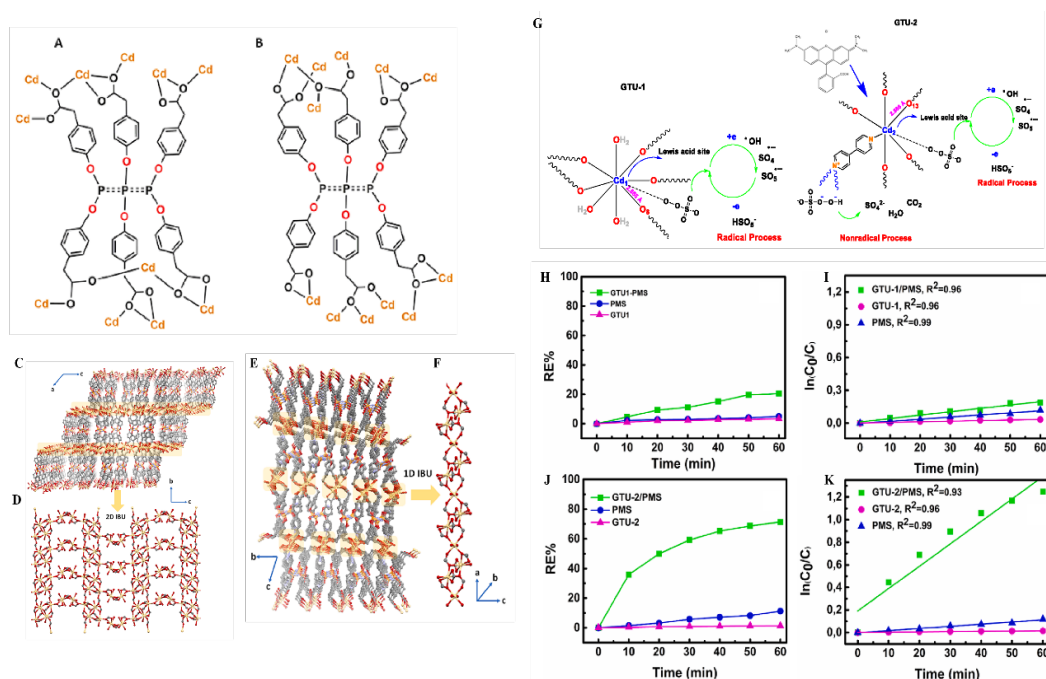


Figure 3.2.: Studies of CP GTU-1, GTU-2 [51].

strong thermal stability, rendering them very suitable for applications in VOC sensing. Fluorescence experiments have shown that compound 1, one of the produced compounds, can work as a versatile fluorescence sensor for VOCs such as salicylic aldehyde, furfural, and benzaldehyde. It exhibits distinct fluorescence emission characteristics for each of these chemicals. In addition, the study effectively synthesized a range of Dye@La-HCPCP composites (Dye = rhodamine B, safranin T, crystal violet, and malachite green) via a solvothermal reaction followed by cation exchanges. This process resulted in different quantum yields and adjustable emission colors. The Ln-MOFs were synthesized by solvothermal processes, wherein lanthanide salts and the HCPCP ligand were mixed in the presence of DMA and HNO_3 to regulate the pH. The crystals obtained were analyzed using several techniques including FT-IR spectroscopy, TGA, SEM, PXRD, and SCXRD. The study discovered that the compounds demonstrated exceptional thermal stability, as their breakdown temperatures exceeded 330°C . Additionally, the PXRD patterns verified that the crystalline structures remained consistent both before and after the sensing tests. Fluorescence sensing studies demonstrated that compound 1 had an increase in fluorescence intensity when exposed to salicylic aldehyde, but a decrease in fluorescence intensity when exposed to furfural. In contrast, benzaldehyde had minimal influence on the fluorescence intensity. The observed behaviors were ascribed

to the distinct interactions between the aldehydes and the HCPCP ligand. The study suggested that the hydroxyl group in salicylic aldehyde forms an interaction with the HCPCP ligand, causing a rise in fluorescence. On the other hand, the furan ring in furfural enables electron transfer, which leads to the quenching of fluorescence. The study also examined the fluorescence reaction of compound 1 to several volatile solvents. It discovered that solvents containing electron-withdrawing groups, such as CHCl_3 and CH_2Cl_2 , resulted in substantial reduction in fluorescence. The Dye@La-HCPCP composites were created by submerging La-HCPCP powders in DMA solutions containing various dyes. This process led to alterations in color and adjustable emission properties. The fluorescence intensities and emission colors of the composites were manipulated by altering the amounts of the dyes and the wavelengths of stimulation, showcasing potential uses in solid-state fluorescent materials. The work effectively created and analyzed a range of Ln-MOFs that have the potential to be used in VOC sensing and the encapsulation of fluorescent dyes. The results emphasize the significance of adaptable, versatile ligands such as HCPCP in improving the effectiveness of MOFs in many environmental and material science applications. This research serves as a helpful point of reference for future studies on the design and implementation of Ln-MOFs in fluorescence sensing and the creation of composite materials with adjustable colors [35].

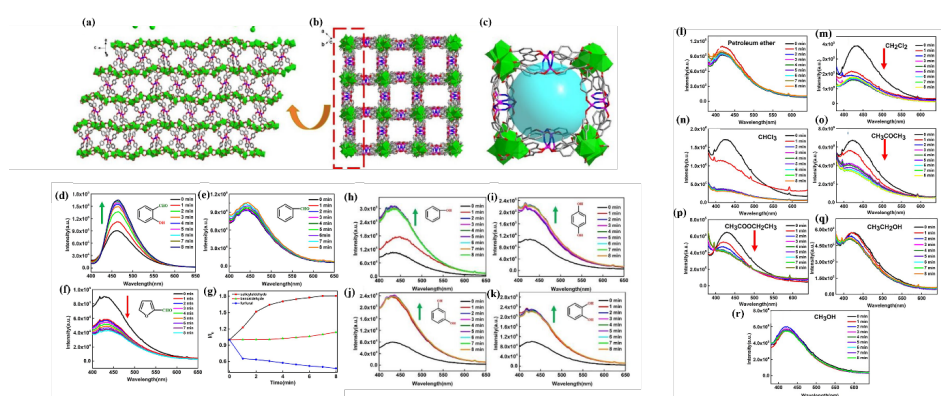


Figure 3.3: (a) 2D layers SBUs and the organic ligands [35].

The study conducted by Bao Li centers around the creation of a new MOF that demonstrates versatile sensing abilities, namely in detecting color changes when exposed to ketone molecules. The scientists utilized a hexadentate ligand generated from cyclotriphosphazene, which is recognized for its spiral topologies and ability to interact in numerous ways, to create the MOF through a simple synthesis technique

using inexpensive raw ingredients. This MOF exhibits distinctive solvochromic sensing properties towards tiny ketone molecules such as acetone, acetophenone, and 2,5-diketohexane. The helical channels included in the manganese-carboxylate chain structure of the MOF provide a substantial pore volume, facilitating the adsorption of large organic molecules and the separation of 1-phenyl -EtOH with high enantiopure selectivity, achieving an enantiomeric excess (ee) of 35.99%. The synthesis procedure entailed the amalgamation of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and the hexacarboxylate ligand H_6L_1 in a solution comprising DMF and water, subsequently followed by the introduction of HNO_3 . The crystals obtained were analyzed by SCXRD, elemental analysis, PXRD, and TGA. The MOF, also known as 1, has a 3D porous structure with 1D helical Mn chains and hexacarboxylate bridges. It crystallizes in an orthorhombic chiral space group. The structural investigation verified that the framework is composed of Mn(II) centers linked by carboxylate groups in different coordination modes, resulting in a stable and porous structure with the ability to host guest molecules. The solvochromic behavior of the MOF crystals was examined by submerging them in different solvents. This investigation unveiled that the framework undergoes a color shift when exposed to ketone molecules. Acetone, acetophenone, and 2,5-diketohexane had a distinct red color alteration, whilst MeOH, CH_3CN , and CHCl_3 had no impact on the hue. The solvochromic phenomena is caused by the robust H-bonding connections between the ketone molecules and particular locations inside the helical channels of the MOF. The inclusion of acetophenone within the MOF was further examined using SCXRD, which verified the preservation of crystalline structure and offered understanding into the alterations in the arrangement that caused the alteration in color. In addition, the MOF exhibited the ability to selectively separate 1-phenyl EtOH in an enantiopure manner. The researchers achieved chiral separation by submerging the MOF in a racemic mixture of 1-phenyl EtOH, extracting and analyzing it. They found that the MOF had an ee value of 35.99%, indicating its potential for chiral separation applications. The presence of both solvochromic sensing and chiral separation capabilities in a single MOF material is uncommon and highlights the versatility of the proposed framework. The work effectively created a versatile MOF that exhibits unique solvochromic properties specifically towards ketone molecules and has the capability to selectively separate enantiopure substances. The findings emphasize the significance of logical ligand design and structural

configuration in producing sophisticated materials with numerous sensing capabilities. This research enhances the field of MOFs by presenting a unique material that combines solvochromic sensing with chiral separation. It provides vital insights for the future advancement of multifunctional sensing materials [50].

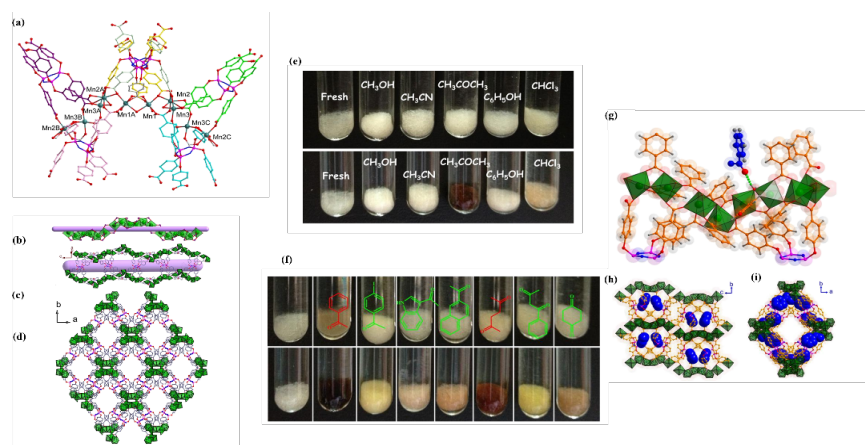


Figure 3.4: (a) Perspective view of interconnection mode [50].

The study conducted by Yajing Ling centers on the creation, production, and examination of a new lanthanide MOF (Ln-MOF) employing a versatile cyclotriphosphazene-functionalized hexacarboxylate ligand. The work investigates the specific gas adsorption capabilities of the synthesized Ln-MOF, specifically its capacity to selectively adsorb C_2 hydrocarbons over CH_4 at ambient temperature, emphasizing its potential use in natural gas purification. The Ln-MOF was prepared via a solvothermal technique by mixing hexakis(4-carboxylatephenoxy)cyclotriphosphazene (H_6L), holmium nitrate hexahydrate ($Ho(NO_3)_3 \cdot 6H_2O$), and thiophene-2,5-dicarboxylate in a combination of N,N -DMA and (H_2O). HCl was used as a modulator. The crystals obtained were analyzed using SCXRD, PXRD, FT-IR, TGA, and gas adsorption isotherms. The SCXRD study determined that the Ln-MOF crystallizes in a monoclinic system with a chiral space group. It forms a 3D structure with rod-shaped SBUs that are connected by flexible organic ligands. The framework comprises sinistral helical chains of Ho^{3+} ions linked by the ligand's carboxylate groups, resulting in 1D channels that are filled with solvent molecules and dimethylammonium counterions. The desolvated Ln-MOF, known as ZJNU-61a(Ho), displayed enduring porosity, as proven by N adsorption isotherms at 77 K. It had a BET surface area of $1059 \text{ m}^2/\text{g}$ and a total pore volume of $0.456 \text{ cm}^3/\text{g}$. The gas adsorption studies revealed that ZJNU-61a(Ho) exhibits selective adsorption

of C₂ hydrocarbons (acetylene, ethylene, and ethane) over CH₄, with notable variations in adsorption capabilities at a temperature of 298 K and a pressure of 1 atm. The calculations of the isosteric heat of adsorption (Q_{st}) revealed that C₂ hydrocarbons have a stronger attraction compared to CH₄. This can be related to the size of the framework's pores and the existence of open metal sites and heteroatoms, which increase the binding energy. The study additionally evaluated the thermal stability of ZJNU-61(Ho) using TGA and variable-temperature PXRD, verifying its stability up to 733 K in a N atmosphere. Gas adsorption experiments conducted at different temperatures shown that the framework retained

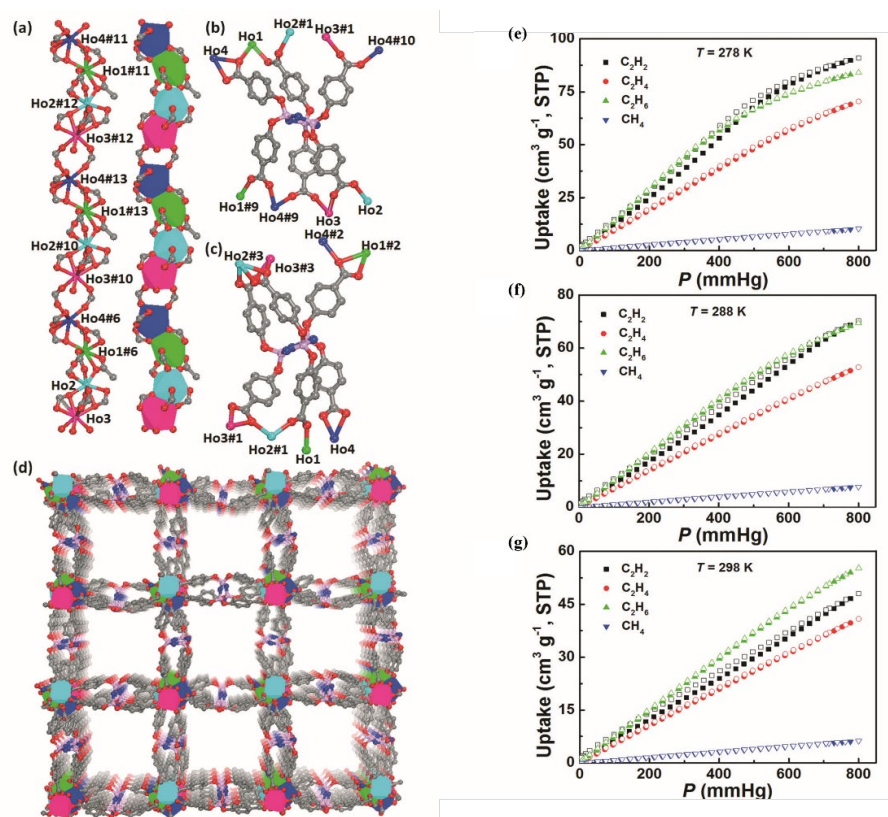


Figure 3.5: Studies of CP Ho-MOF [37].

its porosity and structural integrity, rendering it ideal for practical utilization in gas separation and purification. The study showcases a unique instance of a persistently porous Ln-MOF built using a flexible ligand, demonstrating selective gas adsorption characteristics. The results highlight the capacity of cyclotriphosphazene-functionalized ligands to produce durable and efficient Ln-MOFs for use in environmental and industrial contexts. This study enhances the continuous endeavors to create sophisticated materials for gas separation, providing valuable knowledge on

how to design and produce multifunctional MOFs with customized characteristics. The effective creation and analysis of ZJNU-61a(Ho) emphasizes the significance of the ability of ligands to move and the science of coordinating atoms in order to achieve specific material properties. This opens up opportunities for further exploration and advancement in the field of MOFs [37].

The study authored by Beibei Li, introduces a novel sensor designed for the ratiometric detection of trace water in CH₃CN. The study emphasizes the significance of MOFs due to their highly ordered structures, chemically adjustable porosities, and high surface areas, making them suitable for various applications, including gas storage, catalysis, and chemical sensing. The MOFs Tb-L1 and Eu-L1

were synthesized using Tb(NO₃)₃·6H₂O or Eu(NO₃)₃·6H₂O, HCPCP (H₆L₁), and acetic acid under solvothermal conditions, resulting in colorless crystals [49].

SCXRD analyses revealed that Tb-L1 and Eu-L1 are isomorphous and crystallize in the monoclinic system with the space group C₂/c. These structures consist of 3D rod-packing frameworks where each Tb³⁺-carboxylate infinite SBU is connected to four others through the cyclotriphosphazene portion of H₆L₁. The bimetallic lanthanide Tb_{0.97}Eu_{0.03}-L1 was synthesized by varying the M ratios of Tb(NO₃)₃·6H₂O to Eu(NO₃)₃·6H₂O, and its structure was confirmed to be isostructural with Tb-L1 and Eu-L1 through PXRD. The luminescence properties of Tb-L1 and Eu-L1 were investigated in dry CH₃CN, exhibiting strong characteristic transitions for Tb³⁺ and Eu³⁺ ions upon excitation at 280 nm. The study demonstrated that H₆L₁ is an effective sensitizer for Tb³⁺ and Eu³⁺ based on the antenna effect, with Tb-L1 showing a higher emission intensity than Eu-L1. Upon adding water to the CH₃CN solutions, the luminescence intensities of Tb-L1 and Eu-L1 initially increased due to the formation of H bonds between water and the coordinated H₂O, lowering the energy transfer from the excited state of lanthanides to the O–H oscillators. However, as the water content further increased, the emission intensities of the lanthanide ions decreased, while the fluorescence intensity of the ligand increased. This was attributed to the additional coordination of H₂O with the lanthanide ions, reducing the energy transfer efficiency from the ligands to the lanthanide ions. For ratiometric sensing, Tb_{0.97}Eu_{0.03}-L1 was used to measure water content in CH₃CN. The mixed-lanthanide sensor exhibited variable colors at different water contents, observable under UV light. The emission spectra showed a linear relationship between the fluorescence intensity ratios

(I543/I615) and water content from 0% to 2.5% (v/v%), with a detection limit as low as 0.04%. The sensor displayed an excellent linear regression equation, indicating its potential for quantitative determination of trace water in an organic solvent. Moreover, Tb97.11Eu2.89-L1 exhibited good selectivity for water over other organic solvents such as MeOH, N,N-DMF, and DMSO, with significant differences in luminescence colors and I543/I615 ratios. The sensor also demonstrated reversible fluorescence color changes after absorbing and releasing H₂O, confirming its suitability as a sensitive and reusable water detector [49].

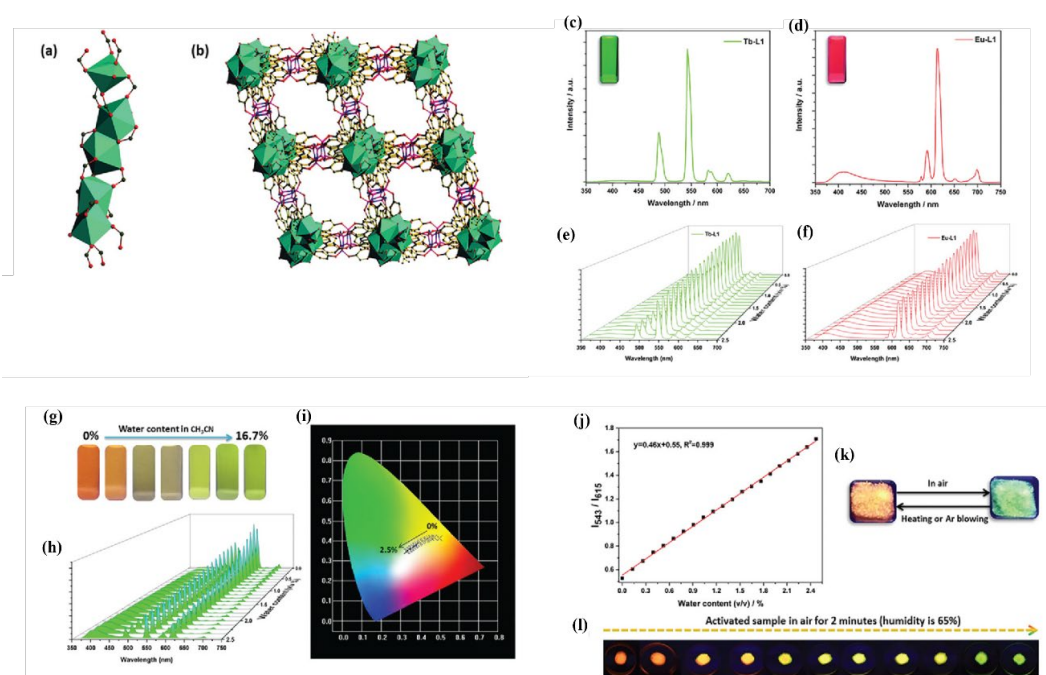


Figure 3.6: Crystal structure of CP [49].

The study successfully developed a new bimetallic lanthanide MOF sensor Tb97.11Eu2.89-L1 that enables ratiometric fluorescence detection of trace water in organic solvents. The sensor's variable emission colors, excellent linear relationship with water content, high sensitivity, selectivity, and reversibility highlight its potential application in industrial processes and environmental monitoring for the detection and quantification of low water levels. The findings contribute to the advancement of MOF-based luminescent materials for chemical sensing applications.

4. MATERIALS AND METHODS

FT-IR spectra of the as-synthesized compounds were recorded in the 600–4000 cm^{-1} range employing a PerkinElmer 100 FT-IR spectrometer. Simultaneous TG curves were obtained under airflow at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ using a Mettler Toledo TGA/SDTA851e analyzer. The XRD patterns were obtained using a Bruker D8 Advance diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The scanning covered a range of 2° to 50° for the scattering angle (2θ), maintaining a scanning speed of $6^{\circ}/\text{sec}$. The X-ray tube operated at a constant 40 kV and 40 mA for both voltage and current. The surface morphology of the CPs was measured using a JEOL JSM-7800F and a JEOL JEM-2100F. The emission spectrum of the solid state of compounds was determined at room temperature using a Varian Cary Eclipse fluorescence spectrophotometer.

Data for **PCP-3**, **PCP-4**, **PCP-5**, and **PCP-6** were performed on a Bruker APEXII CCD diffractometer ($\lambda = 0.71073 \text{ \AA}$). Indexing, data collection, data reduction [53] and absorption correction [54] were carried out using [55]. Crystal structures were solved using SHELXT [56] and then refined by full-matrix least-squares refinements on F2 using the SHELXL [57]. A solvent mask was calculated [58], and 368 electrons in **PCP-3** were found in a volume of $1458 \text{ \AA}^3$ in one void per unit cell. This aligns with the existence of with the presence of four DMF and three H_2O per formula unit which account for 380 electrons per unit cell. In **PCP-4**, A solvent mask was calculated, and 320 electrons were found in a volume of $1442 \text{ \AA}^3$ in two voids per unit cell. This is consistent with the presence of one DEF and two H_2O per formula unit which account for 304 electrons per unit cell. The solvent mask in **PCP-5** was estimated, and 676 electrons were found in a volume of $2856 \text{ \AA}^3$ in three voids per unit cell and this is compatible with the existence of two DMF per formula unit which account for 640 electrons per unit cell. **PCP-6** was analyzed, revealing a solvent mask with a total of 1128 electrons occupying a space of $4052 \text{ \AA}^3$ in per unit cell, which is consistent with the presence of five DEF and one H_2O . The contents of guest molecules are not included in the formula of the final CIF file. Table 1 provides the crystallographic data and refinement information of the data collection. CCDC reference numbers 2350288, 2350289, 2350290, and 2350291 for **PCP-3**, **PCP-4**, **PCP-5**, and **PCP-6** have been

deposited within the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/deposit.

4.1. Used Chemicals in Laboratory Process

Chemical substances used in synthesis, separation, purification and characterization processes are given in Table 4.1.

Table 4.1: Chemical substances used within the scope of the thesis.

Chemical	Supplier	Purity	Usage
$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	Aldrich	Reagent-grade	Precursor for PCPs
phen	Aldrich	Reagent-grade	N-donor ligand for PCP-3
trp	Synthesis		N-donor ligand for PCP-4
2,2'-bpy	Aldrich	Reagent-grade	N-donor ligand for PCP-5
4,4'-bpy	Aldrich	Reagent-grade	N-donor ligand for PCP-6
$\text{N}_3\text{P}_3\text{Cl}_6$	Aldrich	Reagent-grade	Ligand synthesis
MB	Aldrich	Reagent-grade	Dye for photocatalytic testing
MO	Aldrich	Reagent-grade	Dye for photocatalytic testing
RhB	Aldrich	Reagent-grade	Dye for photocatalytic testing
RO16	Aldrich	Reagent-grade	Dye for photocatalytic testing
DMF	Aldrich	Reagent-grade	Solvent for synthesis
DEF	Aldrich	Reagent-grade	Solvent for synthesis
DCM		Reagent-grade	Solvent for synthesis
Hexane		Reagent-grade	Solvent for purification
Methyl-4-hydroxy benzoate	Aldrich	High purity	Ligand used in PCPs

4.2. Used Devices in Laboratory Process

The devices used in the synthesis of the obtained compounds and in elucidating their structures are given in Table 4.2.

Table 4.2: Devices used within the scope of the thesis.

Name	Model	Location
Rotary Evaporator	Heidolph	GTU
Heated Magnetic Stirrer	Heidolph MR Hei-Standart	GTU
Precision Balance	OHAUS	GTU
NMR Spectrophotometer	Varian Inova 500 MHz	GTU
MALDI-TOF	Bruker Microflex LT	GTU
FT-IR Spectrophotometer	Perkin Elmer 100	GTU
Single Crystal X-Ray Diffractometer	Bruker Smart Apex II Quazar	GTU
Thermogravimetric Analysis	Mettler Toledo TGA/SDTA851e	GTU
UV-Vis Spectrophotometer	Shimadzu UV-1900i	GTU

5.EXPERIMENTAL

All organic reagents, the $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ metal salt, solvents, and dye molecules (MB, MO, RhB, and RO16) were procured in reagent-grade quality and employed without further purification, sourced from reputable commercial suppliers. The synthesis of H_6L ligand followed established modified procedure outlined in the literatures [19]. Crystal forms were attained for **PCP-3**, **PCP-4**, **PCP-5**, **PCP-6**.

5.1. Synthesis Method of H_6L

Synthesis of $\text{H}_6\text{L-E}$

In a synthetic procedure, 2.88 grams of potassium carbonate (20.75 mmol) was introduced into a 30 mL solution of anhydrous acetone, containing 1.84 grams (12.10 mmol) of methyl 4-hydroxybenzoate and 1.00 grams (2.88 mmol) of $\text{P}_3\text{N}_3\text{Cl}_6$. The resulting mixture underwent stirring overnight at 80 °C. Subsequently, the solvent was evaporated under reduced pressure, and the obtained solid was redissolved in 50 mL CH_2Cl_2 . The organic phase underwent washing with water, followed by drying over anhydrous Na_2SO_4 . After removing the volatiles under reduced pressure, the product $\text{H}_6\text{L-E}$ was obtained as a white powder with a yield of 95% based on $\text{P}_3\text{N}_3\text{Cl}_6$. The obtained product was characterized by Mass, ^{31}P NMR, ^1H NMR spectroscopy. MALDI-TOF (m/z) [M^+] 1040.31; ^1H -NMR (400 MHz, CDCl_3 , ppm) 7.87 (d, 12H, Ar-H), 7.01 (d, 12H, Ar-H), 3.94 (s, 18H, CH_3); ^{31}P -NMR (400 MHz, CDCl_3 , ppm).

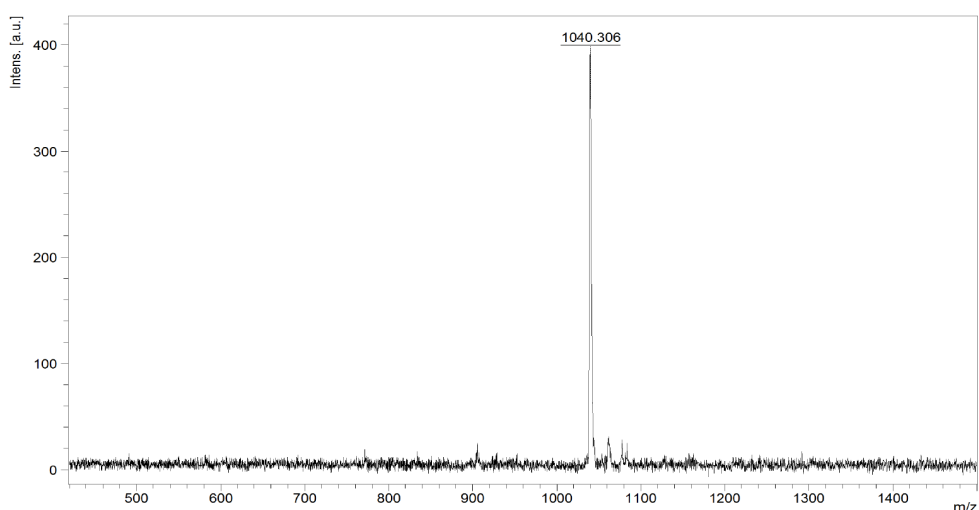


Figure 5.1: Mass spectrum of $\text{H}_6\text{L-E}$.

Synthesis of H₆L

1.11 grams of NaOH (27.84 mmol) dissolved in 75 mL MeOH was combined with 2 grams (1.92 mmol) of H₆L-E. The resulting mixture was stirred overnight at 80°C. After removing volatiles, the residue was dissolved in water, filtered, and acidified to pH ~ 2–3 using dilute HCl. The product precipitated upon stirring, was collected by filtration, washed with water, and dried, resulting in a yield of 97.4% (1.79 g).

The obtained product was characterized by Mass, ³¹P NMR, ¹H NMR and IR spectroscopy MALDI-TOF (m/z) [M⁺] 956.26; ¹H-NMR (400 MHz, DMSO-d₆, ppm) 7.83 (d, 12H, Ar-H), 7.00 (d, 12H, Ar-H); ³¹P-NMR (400 MHz, DMSO-d₆, ppm) (s, 7.99). IR (ATR): ν/cm⁻¹ 3081.4, 2952.2, 2666.6, 2537.0, 2103.7, 1692.7, 1601.7, 1504.7, 1421.9, 1312.9, 1276.1, 1257.5, 1209.4, 1200.3, 1184.2, 1156.2, 1016.7, 980.5, 942.7, 894.8, 879.0, 858.4, 816.2, 801.1, 771.4, 735.5, 717.0, 689.6, 652.9.

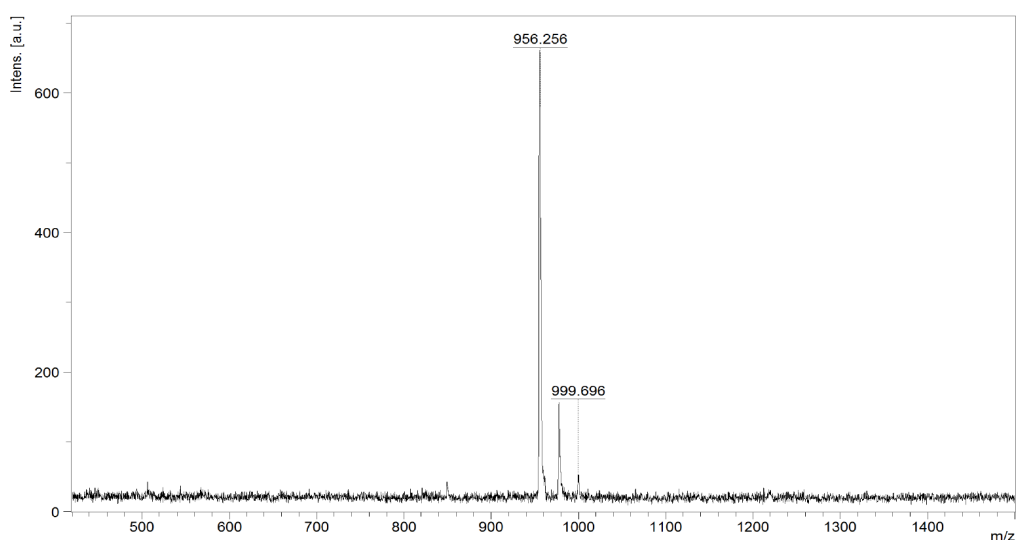


Figure 5.2: Mass spectrum of H₆L.

5.2. Synthesis of PCP-3 [(CH₃)₂NH₂]⁺ [{Cd₆(phen)₂(L₂)(HCOO)(H₂O))}.4DMF.3H₂O

Cd(NO₃)₂·6H₂O (21.60 mg) and H₆L (15 mg) were dissolved in 3 mL of a DMF–H₂O mixture (2:1, v/v). Then 2.82 mg of phen was added. The resulting mixture was ultrasonicated for 15 minutes and subsequently, the final mixture underwent heating at 80°C for 72 hours, followed by cooling to room temperature. The resulting crystals were washed three times with DMF, water, and acetone, then centrifuged. The washed

product was vacuum-dried at 70°C for 12 hours. The CP, **PCP-3**, was characterized using single crystal X-ray and powder X-ray diffraction. A yield of 69%, based on H₆L, resulted in the formation of 18 mg of colourless block crystals of **PCP-3**. IR (ATR): ν cm⁻¹ 3230.1, 3074.0, 2329.6, 2107.6, 1876.1, 1703.2, 1652.8, 1597.3, 1534.5, 1519.8, 1503.2, 1392.3, 1292.6, 1264.6, 1198.4, 1175.2, 1154.6, 1098.5, 1015.0, 947.2, 887.1, 861.8, 849.4, 785.4, 765.6, 744.8, 726.1, 697.6, 659.9. Considering with TGA data, the comprehensive formula for **PCP-3** is proposed as.

5.3. Synthesis of **PCP-4** [**Cd₂(trp)₂(H₂L)**]. **DEF.2H₂O**

Cd(NO₃)₂·6H₂O (21.60 mg) and H₆L (15 mg) were dissolved in 3 mL of a DEF–H₂O mixture (2:1, v/v). Then 3.66 mg of trp was added. The resulting mixture was ultrasonicated for 15 minutes and subsequently, the final mixture underwent heating at 80°C for 72 hours, followed by cooling to room temperature. The resulting crystals were washed three times with DEF, water, and acetone, then centrifuged. The washed product was vacuum-dried at 70°C for 12 hours. The CP, **PCP-4**, was characterized using single crystal X-ray and powder X-ray diffraction. A yield of 54%, based on H₆L, resulted in the formation of 15 mg of colourless block crystals of **PCP-4**. IR (ATR): ν cm⁻¹ 3066.6, 2983.2, 2111.1, 1705.2, 1656.4, 1596.3, 1573.3, 1536.8, 1502.7, 1475.5, 1438.5, 1450.2, 1397.0, 1312.9, 1267.8, 1242.8, 1176.2, 1153.9, 1094.2, 1013.1, 940.6, 885.9, 864.6, 787.0, 768.3, 746.0, 695.1. Considering with TGA data, the comprehensive formula for **PCP-4** is proposed as.

5.4. Synthesis of **PCP-5**

[Cd₃(2,2'-bpy)₂(L)(DMF) (H₂O)]·2DMF

Cd(NO₃)₂·6H₂O (21.60 mg) and H₆L (15 mg) were dissolved in 3 mL of a DMF–H₂O mixture (2:1, v/v). Then 2.44 mg of 2,2'-bpy was added. The resulting mixture was ultrasonicated for 15 minutes and subsequently, the final mixture underwent heating at 80°C for 72 hours, followed by cooling to room temperature. The resulting crystals were washed three times with DMF, water, and acetone, then centrifuged. The washed product was vacuum-dried at 70°C for 12 hours. The CP, **PCP-5**, was characterized using single crystal X-ray and powder X-ray diffraction. A yield of 59%, based on H₆L, resulted in the formation of 17 mg of colorless block crystals of **PCP-5**. IR

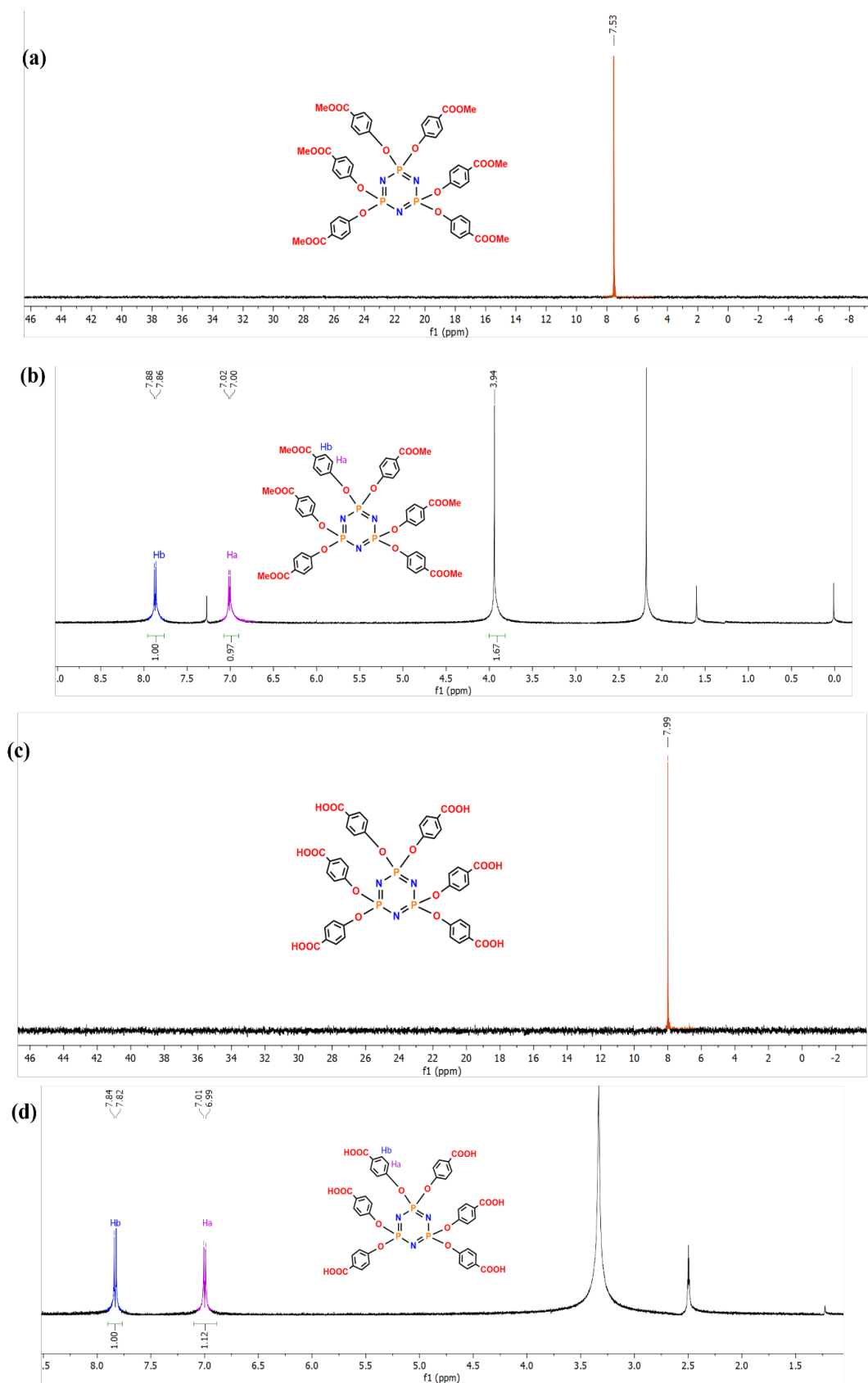


Figure 5.3: ³¹P NMR and ¹H NMR spectrum of H₆L-E and H₆L.

(ATR): ν cm⁻¹ 3241.1, 3070.3, 1651.7, 1597.5, 1533.0, 1503.2, 1475.5, 1438.5, 1392.1, 1318.5, 1292.6, 1266.4, 1200.3, 1176.6, 1154.7, 1097.7, 1059.9, 1015.4, 948.4, 885.2, 861.2, 784.4, 763.1, 697.2. Considering with TGA data, the comprehensive formula for **PCP-5** is proposed as.

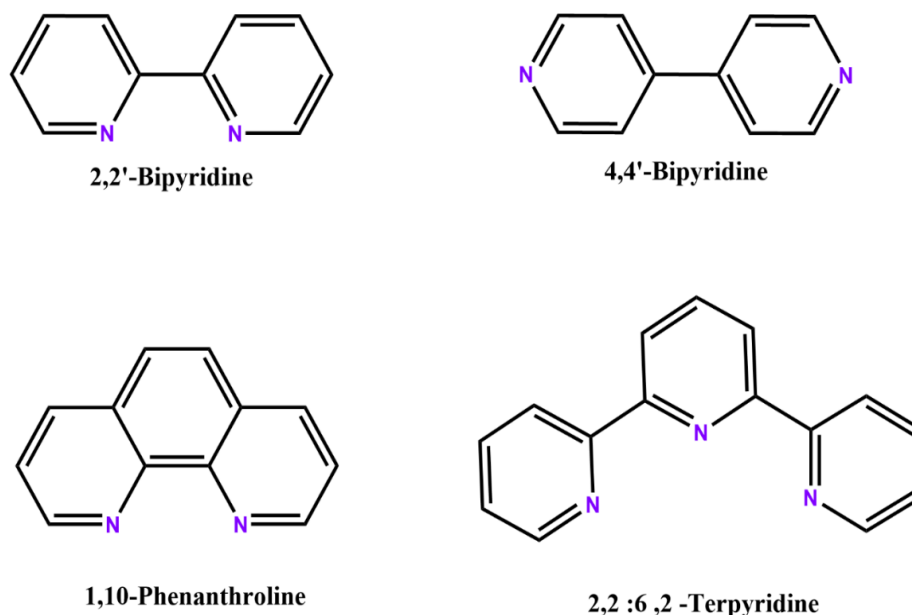


Figure 5.4: Chemical Structure of N-donor ligands.

5.5. Synthesis of PCP-6

[{Cd₆(4,4'-bpy)₂(L₂) (H₂O)₉}. 5DMF.H₂O]

Cd(NO₃)₂·6H₂O (21.60 mg) and H₆L (15 mg) were dissolved in 3 mL of a DMF–H₂O mixture (2:1, v/v). Then 2.44 mg of 4,4'-bpy was added. The resulting mixture was ultrasonicated for 15 minutes and subsequently, the final mixture underwent heating at 80 °C for 72 hours, followed by cooling to room temperature. The resulting crystals were washed three times with DMF, water, and acetone, then centrifuged. The washed product was vacuum-dried at 70°C for 12 hours. The CP, **PCP-6**, was characterized using single crystal X-ray and powder X-ray diffraction. A yield of 43%, based on H₆L, resulted in the formation of 12 mg of colorless block crystals of **PCP-6**. IR (ATR): ν cm⁻¹ 3217.5, 3062.9, 2311.1, 2096.2, 1708.2, 1655.2, 1597.8, 1524.2, 1505.0, 1397.5, 1264.6, 1202.1, 1155.1, 1095.8 1014.6, 973.1, 948.9, 884.8, 862.2, 810.8, 784.1, 764.5, 744.4, 696.9. Considering with TGA data, the comprehensive formula for **PCP-6** is proposed as. Synthetic pathway of H₆L ligand and PCPs and also coordination mode of PCPs were given in Figure 5.7.

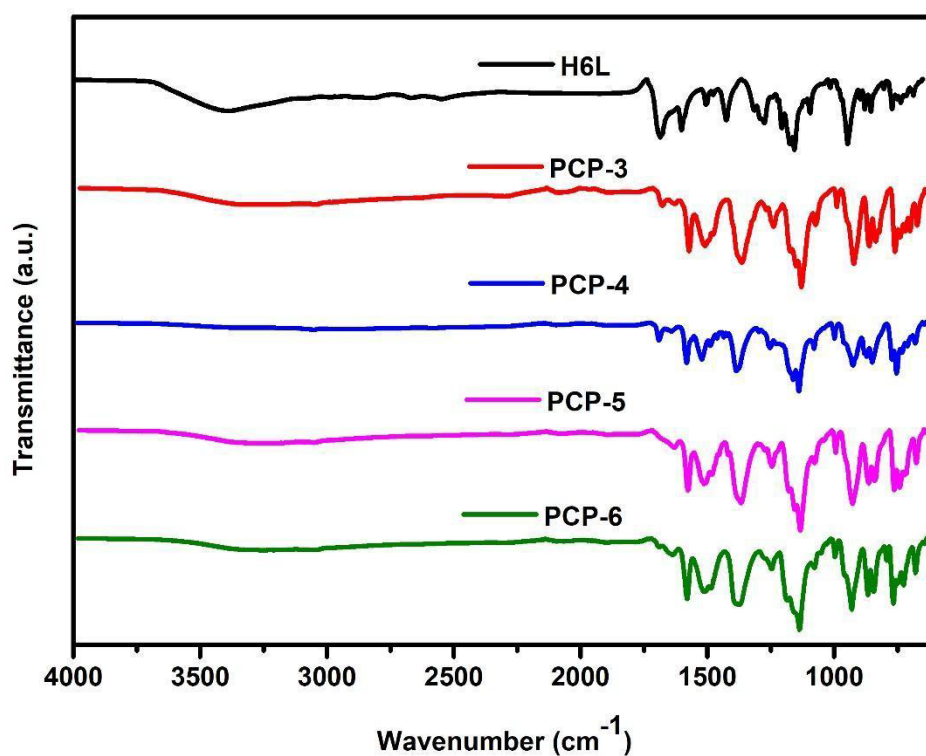


Figure 5.5: FTIR spectrum of H₆L, PCP-3, PCP-4 and PCP-5, PCP-6.

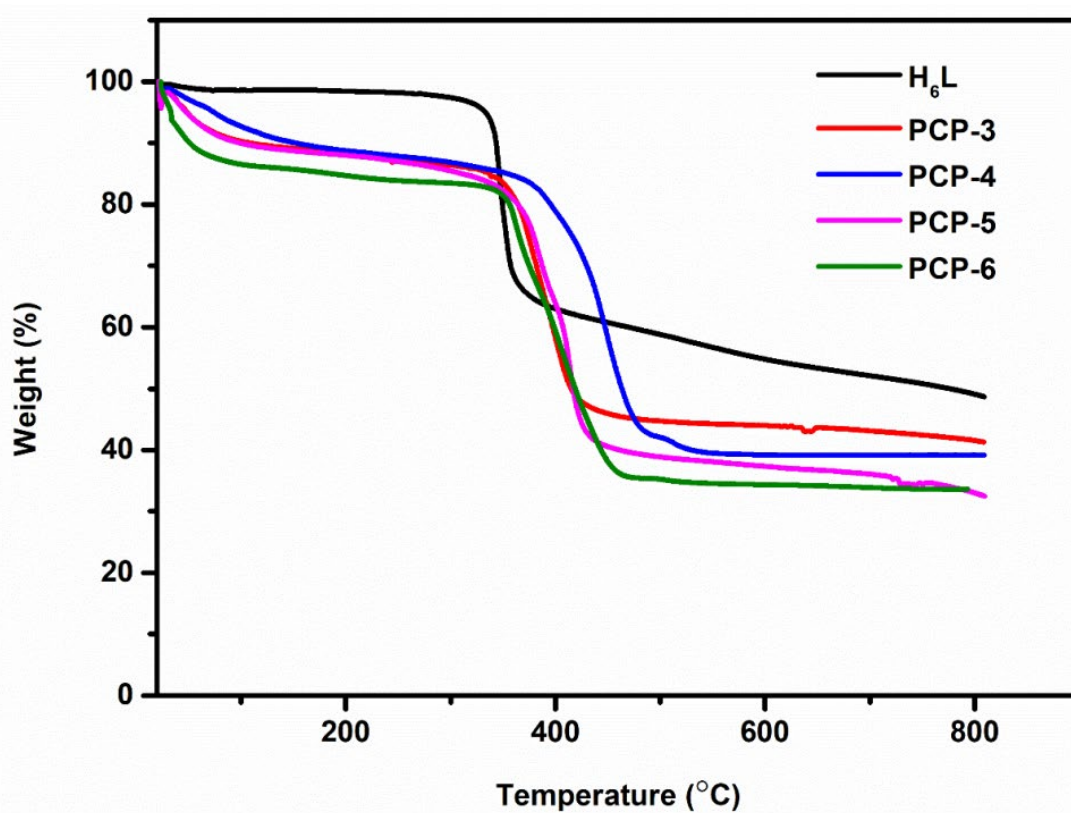


Figure 5.6: TGA of H₆L, PCP-3, PCP-4, PCP-5 and PCP-6.

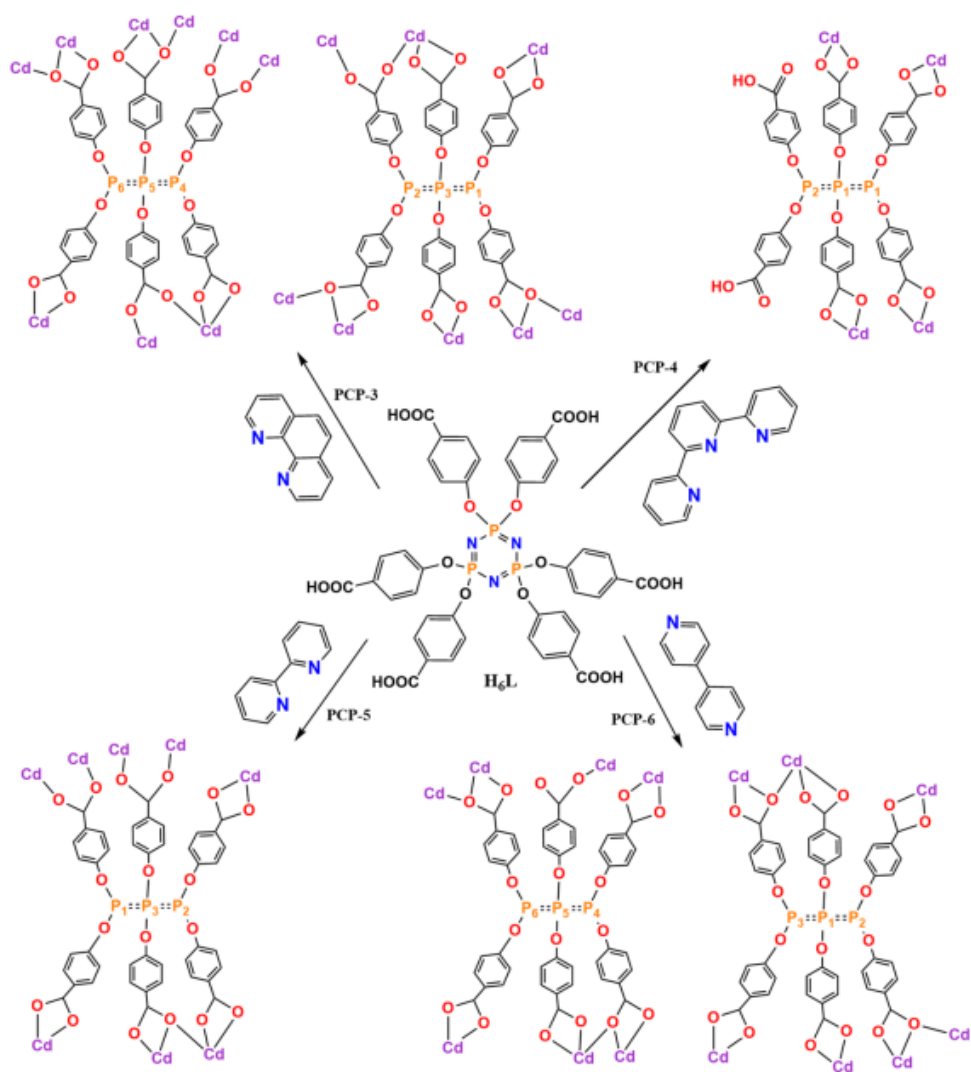


Figure 5.7: Synthetic pathway and coordination mode of PCPs.

Table 5.1: Crystallographic data and structure refinement details for PCPs.

	PCP-3	PCP-4	PCP-5	PCP-6
Empirical formula	C ₁₂₃ H ₁₀₉ Cd ₆ N ₁₅ O ₄₇ P ₆	C ₇₇ H ₆₃ Cd ₂ N ₁₀ O ₂₁ P ₃	C ₇₁ H ₆₃ Cd ₃ N ₁₀ O ₂₂ P ₃	C ₁₂₉ H ₁₃₇ Cd ₆ N ₁₅ O ₅₁ P ₆
Formula Weight (g/mol)	3409.47	1782.08	1838.42	3573.75
Crystal System	Monoclinic	Monoclinic	monoclinic	monoclinic
Space Group	Pc	C2/c	C2/c	C2
a (Å)	16.8481(13)	30.766(6)	32.660(11)	48.513(13)
b (Å)	14.4096(12)	14.870(3)	9.154(3)	11.623(3)
c (Å)	27.232(2)	16.899(3)	51.322(18)	34.319(9)
α (°)	90	90	90	90
β (°)	96.794(2)	90.548(4)	100.695(7)	132.340(4)
γ (°)	90	90	90	90
V (Å ³)	6564.8(9)	7731(3)	15077(9)	14304(6)
Z	2	4	8	4
D _c (g/cm ³)	1.725	1.531	1.620	1.659
μ (mm ⁻¹)	1.122	0.693	0.984	1.036
θ range (deg)	2.826 to 50	3.874 to 49.996	2.538 to 49.998	1.68 to 49.998
Measured Reflections	102946	24881	89488	91286
Independent Reflections	23125	6810	13275	25169
R _{int}	0.0853	0.0560	0.1286	0.3385
S	0.0755	0.0558	0.0865	0.5236
R1/wR2	0.0637 / 0.0862	0.0639 / 0.0942	0.0896 / 0.1530	0.2249 / 0.1918
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (e Å ⁻³)	0.74 / -0.55	0.34 / -0.57	0.69 / -1.15	1.17 / -1.19

5.6. Photocatalytic Reaction Measurement

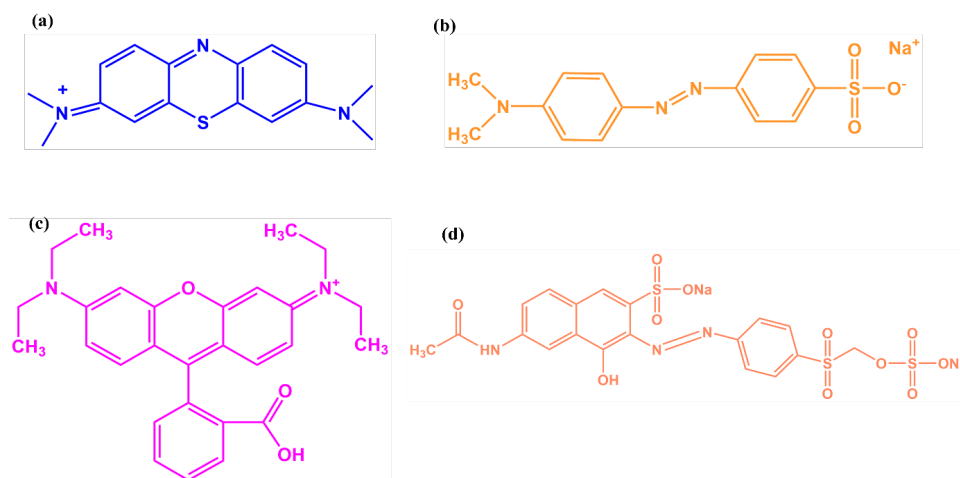


Figure 5.8: Chemical Structure of dyes (a) MB (b) MO (c) RhB (d) RO16.

Photocatalysis experiments were performed in a 250 mL borosilicate glass container under standard atmospheric conditions. The setup involved mechanical stirring and exposure to UVA light (365 nm) from six Philips Actinic BL 8W lamps. The light intensity, gauged at 3.5 mW/cm^2 , was validated using a Lutron UVA-365 light meter. In these experiments, 30 mg of as-synthesized CPs **PCP-3** to **PCP-6** were introduced into 30 ppm of 100 mL dye solutions. The resulting 30 ppm dye/CP suspension underwent a 30-minute stir without light irradiation to achieve adsorption-desorption equilibrium. Subsequently, it was continuously stirred under light exposure for a specified duration. At regular intervals, a 4 mL sample was withdrawn from the reactor, and the catalyst particles were separated via centrifugation. Color removal from the dye solutions was assessed by measuring absorbance using a Hach-Lange DR 3200 photometer at the respective max absorption wavelength (λ_{max}) for each dye. Dye solutions with concentrations ranging from 4 to 20 mg/L were prepared and calibrated using a spectrophotometer. Optimal conditions for degrading MB, MO, RhB, and RO16 were determined by varying catalyst quantity and initial dye concentrations. The identified optimal conditions included a 100 mL dye solution volume, pH levels ranging from 5.0 to 5.5 based on the dye type, and an optimal catalyst loading of 200 mg/L. Photocatalytic removal experiments were conducted at $25^\circ\text{C} \pm 2$. Dye degradation efficiencies were assessed using a UV/vis spectrometer, tracking absorbances at 665 nm for MB, 554 nm for RhB, 463 nm for MO, and 493 nm for

RO16. The degradation kinetics were modeled using a pseudo-first-order equation:

$$\ln(C_0 - C) = kt \quad (5.1)$$

where C_0 is the initial concentration, C is the concentration at a specific time t , k is the degradation rate constant, and t is the reaction time.

Table 5.2: The properties of the dyes.

Chemical Name	Methylene Blue	Rhodamine B	Methyl Orange	Reactive Orange 16
Chemical Form	$C_{16}H_{18}ClN_3S$	$C_{28}H_{31}ClN_2O_3$	$C_{14}H_{14}N_3NaO_3S$	$C_{20}H_{17}N_3Na_2O_{11}S_3$
Molecular weight (g.mol ⁻¹)	319.85	479.01	327.34	617.54
UV absorption λ_{max} (nm)	665	554	463	493
Charge	Cationic	Cationic	Anionic	Anionic

6.RESULTS

6.1. Synthesis and Spectral Characterization

A systematic solvothermal synthesis methodology was employed to fabricate PCPs. The synthesis process involved the careful adjustment of various reaction parameters, including temperature, M ratios of starting materials (metal:ligand:N-donor ligand ratios) and pH (6 M HNO₃: 2:4:5), to achieve the formation of single crystals of PCPs. The experiments utilized a binary solvent system comprising water and DMF.

The role of M ratios of metal:ligand was particularly noteworthy in the crystal formation process. No single crystal product was observed at the ratio of 2:1 (metal:ligand). However, at 4:1 M ratios of metal:ligand, crystals of $[(\text{CH}_3)_2\text{NH}_2]^+[\{\text{Cd}_6(\text{phen})_2(\text{L}_2)(\text{HCOO})(\text{H}_2\text{O})\}].4\text{DMF}.3\text{H}_2\text{O}$ (**PCP-3**), $[\{\text{Cd}_2(\text{trp})_2(\text{H}_2\text{L})\}].\text{DEF}.2\text{H}_2\text{O}$ (**PCP-4**), $[\{\text{Cd}_3(2,2'\text{-bpy})_2(\text{L})(\text{DMF})(\text{H}_2\text{O})\}].2\text{DMF}$ (**PCP-5**), $[\{\text{Cd}_6(4,4'\text{-bpy})_2(\text{L}_2)(\text{H}_2\text{O})_9\}].5\text{DMF}.\text{H}_2\text{O}$ (**PCP-6**) were successfully obtained. Notably, the structures of **PCP-3**, **PCP-4**, **PCP-5** and **PCP-6** demonstrated high stability, preserving their integrity even after undergoing photocatalysis experiments.

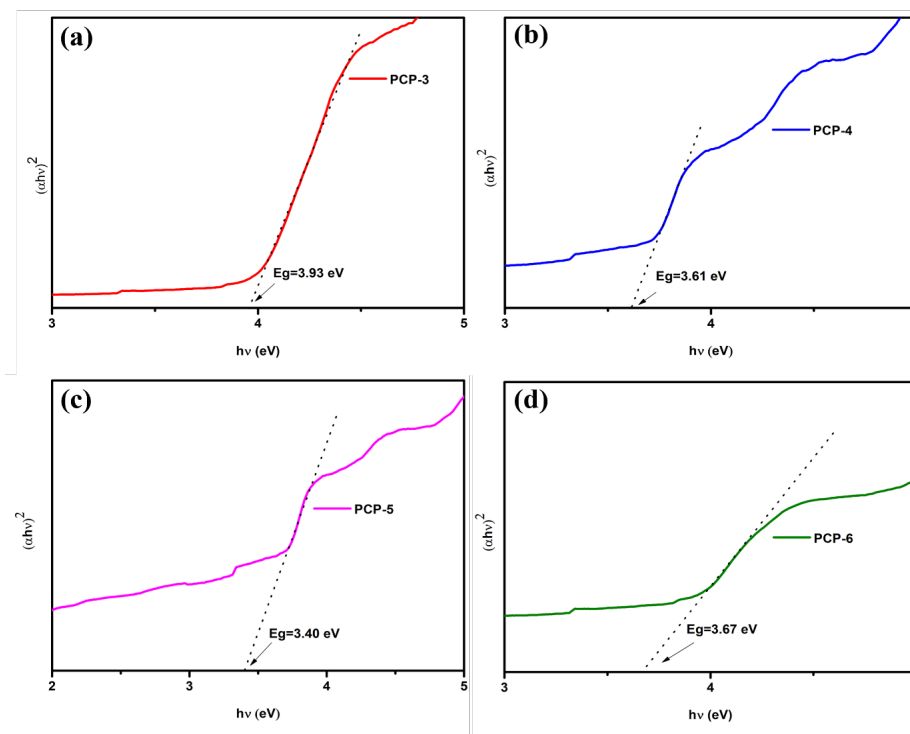


Figure 6.1: (a) K-M Plot of (a) PCP-3, (b) PCP-4, (c) PCP-5, (d) PCP-6.

6.2. FTIR Spectra Analysis

Table 6.1: Selected FT-IR spectral data for Ligand H₆L (cm⁻¹).

Ligand	$\nu(\text{C-H})_{\text{arom.}}$	$\nu(\text{C-H})_{\text{alif}}$	$\nu(\text{C=O})$	$\nu(\text{P=N})$	$\nu(\text{P-O-C})$	$\nu(\text{C=C})$	$\nu(\text{O-H})$
H ₆ L	3081	2952	1693	1206, 1156	1098	1505	3403

FTIR spectrum plays a crucial role in unraveling the molecular characteristics of **PCP-3**, **PCP-4**, **PCP-5**, and **PCP-6**, offering an in-depth analysis of their vibrational modes. For **PCP-3**, the existence of carbonyl groups is discerned through the carbonyl stretching vibration at 1653 cm⁻¹. Furthermore, phosphazene stretching vibrations are evident at two distinct wavenumbers (1198 cm⁻¹ and 1155 cm⁻¹), underscoring the involvement of P-N bonds. The appearance of a peak at 1535 cm⁻¹ corresponds to double bond stretching ($\nu(\text{C=C})$), while the confirmation of aromatic hydrocarbons is indicated by the aromatic C-H stretching vibration at 3074 cm⁻¹. Examining **PCP-4**, the carbonyl stretching vibration manifests at 1656 cm⁻¹, shedding light on the molecule's carbonyl functionalities. Two distinctive phosphazene stretching vibrations emerge at 1207 cm⁻¹ and 1154 cm⁻¹, underscoring the existence of P-N bonds. The double bond stretching vibration ($\nu(\text{C=C})$) at 1537 cm⁻¹ attests to the presence of double bonds, while the aromatic C-H stretching vibration at 3067 cm⁻¹ indicates the existence of aromatic hydrocarbons.

For **PCP-5**, the presence of carbonyl groups is revealed by the carbonyl stretching vibration occurring at 1656 cm⁻¹. Additionally, phosphazene stretching vibrations are observable at two distinct wavenumbers (1200 cm⁻¹ and 1155 cm⁻¹), emphasizing the involvement of P-N bonds. The emergence of a peak at 1533 cm⁻¹ corresponds to double bond stretching ($\nu(\text{C=C})$), while the presence of aromatic hydrocarbons is affirmed by the aromatic C-H stretching vibration at 3070 cm⁻¹.

Examining **PCP-6**, the carbonyl stretching vibration is detected at 1655 cm⁻¹, offering insights into the molecule's carbonyl functionalities. Phosphazene stretching vibrations manifest at two distinct wavenumbers (1202 cm⁻¹ and 1155 cm⁻¹), underscoring the presence of P-N bonds. The presence of double bonds is indicated by the double bond stretching vibration ($\nu(\text{C=C})$) at 1524 cm⁻¹, while the aromatic C-H stretching vibration at 3063 cm⁻¹ confirms the existence of aromatic hydrocarbons.

The FTIR spectrum of H₆L ligand offers crucial insights into their molecular characteristics, revealing distinct features for each. In the FTIR spectrum of H₆L, notable bands include the aromatic C-H stretch band at 3081 cm⁻¹, aliphatic C-H stretch band at 2952 cm⁻¹, carboxyl group stretch band at 1693 cm⁻¹, phosphazene N stretch bands at 1206 cm⁻¹ and 1156 cm⁻¹, P-O-C stretch band at 1098 cm⁻¹, double bond stretch band at 1505 cm⁻¹, and a H-bonded O-H stretch band at 3400 cm⁻¹.

The intricately analyzed FTIR values within the structural characterization section act as distinctive molecular signatures, facilitating a thorough comprehension of the chemical composition and bonding configurations within **PCP-3-6**, and the ligand H₆L. Concise summaries of the FTIR data for both ligand and PCPs can be found in Figure 5.5 and Tables 6.1, 6.2.

Table 6.2: Selected FT-IR spectral data for PCPs (cm⁻¹).

PCP	$\nu(\text{C=O})$	$\nu(\text{P=N})$	$\nu(\text{C=C})$	$\nu(\text{C-H})_{\text{arom.}}$
PCP-3	1653, 1597	1198, 1155	1535	3074
PCP-4	1656, 1596	1207, 1154	1537	3067
PCP-5	1652, 1597	1200, 1155	1533	3070
PCP-6	1655, 1598	1202, 1155	1524	3063

6.3 Crystal Structures

Table 5.1 summarizes the crystal data and structure refinement parameters for **PCP-3-6**. Selected bond distances and bond angles specific to PCPs are provided in Tables Table 5.1. The structural figures were generated using Mercury 3.8 software. While both PCPs share the same unit cells, variations in unit cell parameters reveal distinctive structural characteristics, underscoring nuanced differences.

SCXRD analysis of **PCP-3**, **PCP-4**, **PCP-5**, and **PCP-6** crystallizes in monoclinic unit cell. Figure 6.2 (a) - 6.5 (a) shows the binding modes of the phosphazene ligand and the coordination states of the Cd(II) metal atoms. Figure 6.2 (b) - 6.5 (b) shows the 3D orientation of the MOFs. Figure 6.2 (c) - 6.5 (c) shows the coordination environments and numbers of the Cd(II) metal atoms.

The reaction of $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with H_6L and 4,4'-bpy as divergent N-donor ligand under solvothermal conditions at 80°C afforded a porous CP (Figure 6.2 (a)). Single-crystal X-ray analysis of **PCP-3** crystallizes in monoclinic Pc space group and exhibits

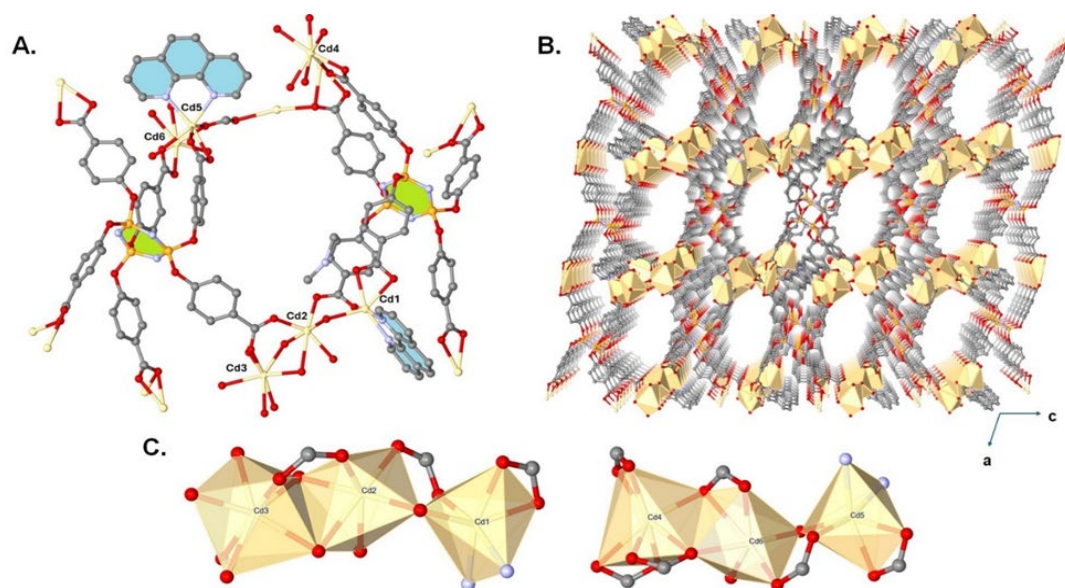


Figure 6.2: (a) Structure of **PCP-3**. (b) View of 3D porous frameworks showing the channel direction along the b-axis. (c) Coordination environment of the six Cd(II) ions in **PCP-3** and view of SBU constructed from trinuclear Cd(II) cluster.

a porous structure with the asymmetric unit containing six Cd(II) cations, two completely deprotonated hexakis(4-carboxylatophenoxy)-cyclotriphosphazene (L) ligands, two phenantroline (phen) ligand, one formate (HCOO^-) anion, and one $[(\text{CH}_3)_2\text{NH}_2]^+$ cation. DMF hydrolysis mediated by metals under solvothermal conditions can produce the HCOO^- and $[(\text{CH}_3)_2\text{NH}_2]^+$ cations. Interestingly, the crystal structure of **PCP-3** consists of two similar inorganic SBUs $\{\text{Cd}_3\text{O}_{14}\text{N}_2\}$ formed by constructed from trinuclear Cd(II) cluster (Figure 6.2 (c)). The Cd1 central atom has a distorted octahedral coordination geometry (CdO_4N_2) composed of three carboxylate oxygen atoms (O_{21} , O_{22} , O_{24}), two nitrogen atoms (N_8 and N_9) of phen, and oxygen atom (O_{25}) of axially weakly coordinated aqua ligand. Cd2 ion is octa-coordinated by five carboxylate oxygen atoms (O_1 , O_2 , O_3) and one aqua oxygen atom (O_{25}) from three different carboxylate groups. Cd3 adopts a pentagonal bipyramidal geometry by six carboxylate oxygen atoms (O_{27} , O_{35} , O_{38} , O_{39} , O_{40} , O_{41}) and one formate oxygen atom (O_{20}). Cd4 ion is occupied by seven carboxylate oxygen atoms (O_{28} , O_{29} , O_{30} , O_{31} , O_{32} , O_{36}). Cd5 ion is in a distorted octahedral geometry through three carboxylate oxygen atoms (O_{14} , O_{15} , O_{17}), one formate oxygen (O_{18}), and two

nitrogen atoms (N₁₀, N₁₁) of phen ligand. Finally, Cd₆ center atom is in a distorted octahedral geometry by four carboxylate oxygens (O₁₆, O₃₀, O₃₆, O₃₇), one formate oxygen atom (O₁₈), and one aqua ligand (O₁₉). In PCP₃, the twelve carboxylate groups of the two ligands in the asymmetric unit are completely deprotonated and actively engage in coordination with the Cd(II) cations exhibiting the syn-syn symmetric chelating (μ_2 - η_1 : η_1), chelating bridging (μ_2 - η_2 : η_1), syn-anti bridging (μ_2 - η_1 : η_1), and syn-syn bridging (μ_2 - η_2 : η_1) coordination modes, as indicated in Scheme 1. **PCP-3** has channels (Figure 6.2 (b)) with diameters of approximately $9.4 \times 12.3 \text{ \AA}^2$, within which dimethyl ammonium is situated. The overall accessible volume for **PCP-3**, after removing guest molecules, is 21.04% as determined by the PLATON software. **PCP-3** material possesses a substantial void volume, which is anticipated to be advantageous for gas storage and separation purposes.

Colourless single crystals of **PCP-4** are solvothermally synthesised using a mixed ligand of H₆L and a terp-pincer type ligand. Crystal structure analysis exhibits that **PCP-4** crystallizes in the monoclinic space group P2₁/n and has a porous π - π stacking framework (Figure 6.3 (b)) involving the 1D tubular channels (Figure 6.3 (c)) with diameters of approximately $7.4 \times 7.7 \text{ \AA}^2$ along the c-axis. The asymmetric unit of **PCP-4** consists of one Cd(II) ion and half a partially deprotonated ligand phosphazene-based ligand (H₂L) with its numbering scheme (Figure 6.3 (a)). Unlike other complexes, the building blocks in **PCP-4** provide an overall -4 net negative charge, which means that it will balance the charge with two Cd(II) metals in the complex system. The Cd(II) center in **PCP-4** was produced by blocking the three coordination sites of the hepta-coordinated Cd(II) center with terp ligand to leave four possible sites for cyclotriphosphazene-functionalized multicarboxylate.

The Cd₁ metal center is hepta-coordinate with a N₃O₄ donor set by three N atoms of the terp ligand and four carboxylate oxygen atoms with syn-syn symmetric chelate coordination modes. In **PCP-4**, the ligand adopts μ_4 coordination binding mode to form a 1D tubular channel-like structure along the c-axis (Figure 6.3 (b)). It is worth noting that the tubular-channel is further expanded into a 3D π - π stacking framework by strong and moderately strong $\pi \cdots \pi$ stacking interactions

($d(\pi \cdots \pi) = 3.766 \text{ \AA}$ and $3.984 \text{ \AA}$) between conjugated terp moieties along b-axis. The overall accessible volume for **PCP-4**, after removing guest molecules, is 17.3%. The

porous π - π stacking framework is further stabilized through five C—H $\cdots$ O interactions, namely, C4—H4 $\cdots$ O6 ($d(\text{H}\cdots\text{O}) = 2.665 \text{ \AA}$), C7—H7 $\cdots$ O6, $d(\text{H}\cdots\text{O}) = 2.571 \text{ \AA}$), C28—H28 $\cdots$ O6, $d(\text{H}\cdots\text{O}) = 2.629 \text{ \AA}$), C3—H3 $\cdots$ O8, $d(\text{H}\cdots\text{O}) = 2.528 \text{ \AA}$), and C13—H13 $\cdots$ O2, $d(\text{H}\cdots\text{O}) = 2.687 \text{ \AA}$), and one classical O—H $\cdots$ O interaction (O8—H8 $\cdots$ O2, $d(\text{H}\cdots\text{O}) = 1.843 \text{ \AA}$).

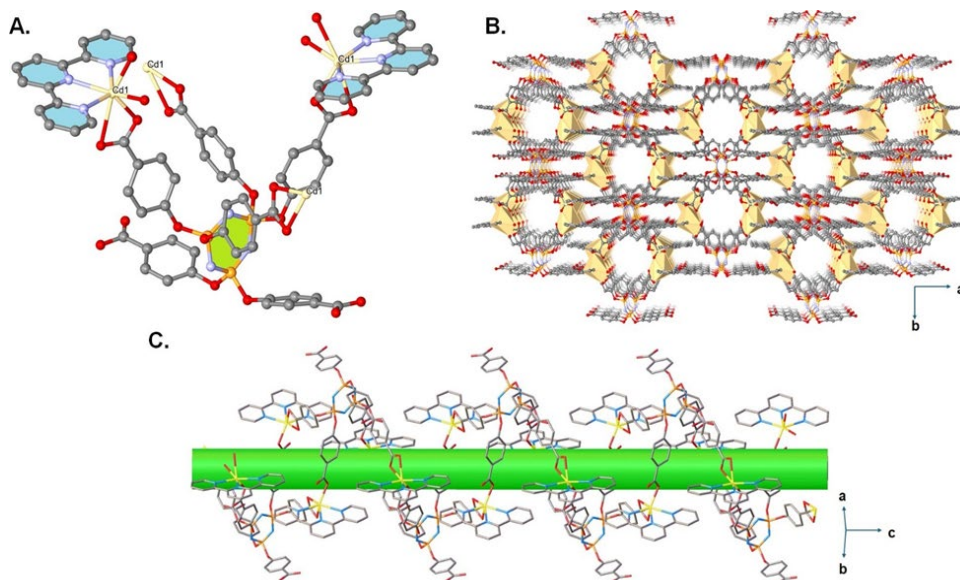


Figure 6.3: (a) Structure of **PCP-4**. All H-atoms were omitted for clarity. (b) View of a porous π - π stacking framework in **PCP-4**. (c) Perspective view of the 1D tubular channels with diameters of approximately $7.4 \times 7.7 \text{ \AA}^2$ along the c-axis.

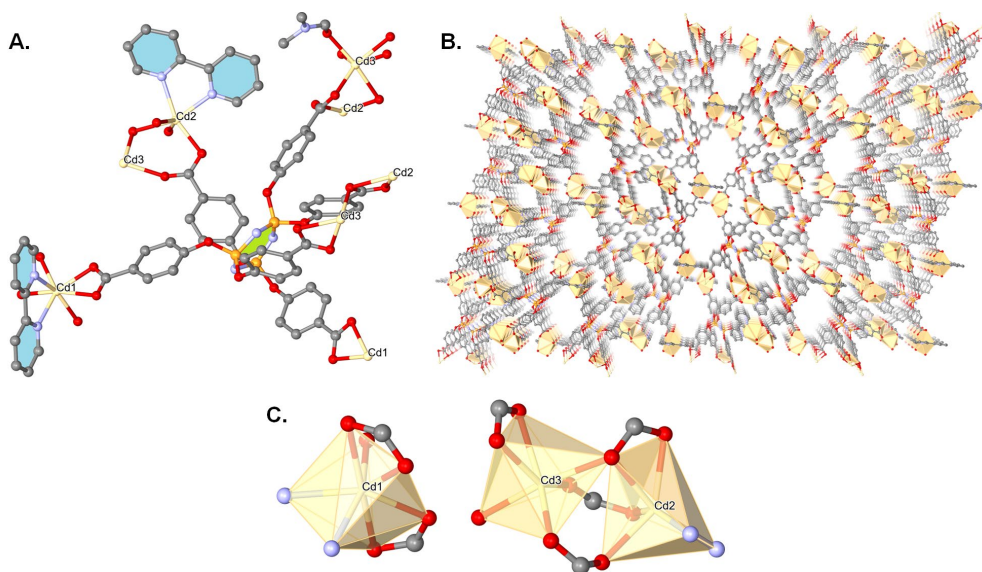


Figure 6.4: (a) Structure of **PCP-5**. All H-atoms were omitted for clarity. (b) View of a porous framework in **PCP-5**. (c) View of coordination environment of the Cd(II) ions in **PCP-5**.

The reaction of the same Cd(II) salt and hexacarboxylate ligands (H₆L) with the N-chelating ligand (2,2'-bpy) has produced **PCP-5** (Figure 6.4 (a)), which also exhibit a 2D framework. **PCP-5** crystallizes in monoclinic space group C2/c, along with three Cd(II) ions (Figure 6.4 (c)), one completely deprotonated ligand (L), two 2,2'-bpy pincer ligands, one coordinated aqua molecule. The Cd₁ atom adopts a pentagonal bipyramidal geometry by two N atoms (N₁ and N₂) of 2,2'-bpy, and four carboxylate oxygen atoms (O₁, O₂, O₁₇, O₁₈), and one aqua ligand. The Cd₂ metal atom is coordinated by two N atoms (N₃ and N₄) of 2,2'-bpy and four carboxylate oxygens (O₄, O₈, O₁₉, O₂₉) to give a distorted octahedral geometry. The Cd₃ atoms is also distorted octahedral geometry through five carboxylate oxygens (O₅, O₇, O₁₅, O₁₆, O₁₉) and one oxygen atom (O₆) of DMF molecule. The phosphazene-based hexacarboxylate ligand connects eight Cd(II) ions by three syn-syn symmetric chelating ($\mu_2\text{-}\eta^1\text{:}\eta^1$), two syn-syn bridging ($\mu_2\text{-}\eta^2\text{:}\eta^1$), and one chelating bridging ($\mu_2\text{-}\eta^2\text{:}\eta^1$) coordination modes to form a 2D layered framework. The resulting 2D layers are extended into a 3D supramolecular network through $\pi\cdots\pi$ stacking interactions ($d(\pi\cdots\pi) = 4.194 \text{ \AA}$). **PCP-5** has channels (Figure 6.4 (b)) with diameters of approximately $8.9 \times 16.9 \text{ \AA}^2$ and the overall accessible volume for **PCP-4**, after removing guest molecules, is 17.0%.

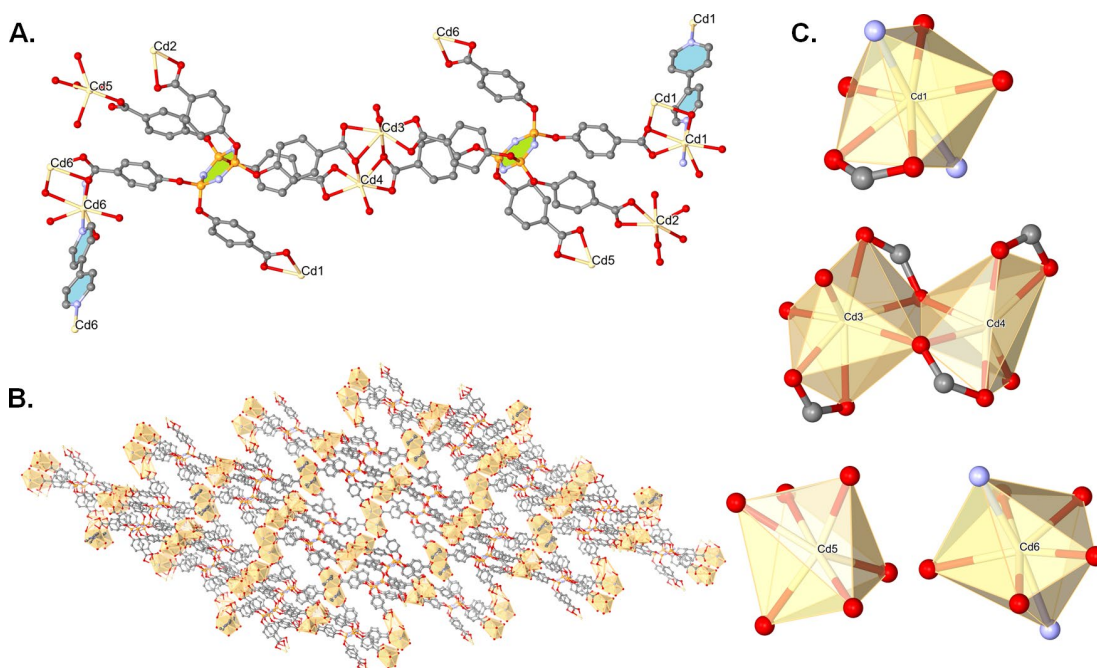


Figure 6.5: (a) Structure of **PCP-6**. All H-atoms were omitted for clarity. (b) View of a porous framework in **PCP-6**. (c) View of coordination environment of the Cd(II) ions in **PCP-6**.

Solvothermal treatment of Cd(II) salt and hexacarboxylate ligands (H₆L) with 4,4'-bpy gave a colourless complex **PCP-6**. The crystal structure of **PCP-6** belongs to the monoclinic crystal system with the C₂ chiral space group. In the asymmetric unit, six Cd(II) ions, two cyclophosphazene-based ligands (L), two 4,4'-bpy pillar ligands, and eight aqua molecules (Figure 6.5 (a)). As illustrated in Figure 6.5 (c), the coordination geometry around Cd₁ and Cd₆ ions can be described as a distorted pentagonal bipyramidal geometry {CdN₂O₅} through five carboxylate oxygens and two pillar N atoms of 4,4'-bpy. The Cd₄ and Cd₅ ions exhibit hexa-coordination, resulting in Cd(H₂O)O₅ and Cd(H₂O)₃O₃ subunits having distorted octahedral geometries, respectively. In contrast, the Cd(H₂O)₃O₄ and Cd(H₂O)₂O₅ units of the seven-coordinated Cd₂ and Cd₃ ions have distorted pentagonal bipyramidal geometry, respectively. Two fully deprotonated cyclophosphazene-based hexacarboxylate linkers (L) exhibits three different fashions, namely, syn-syn symmetric chelating (μ_2 - $\eta^1:\eta^1$), chelating bridging (μ_2 - $\eta^2:\eta^1$) and syn monodentate coordination binding modes, and each ligand connects seven Cd(II) ions to form a 3D porous framework, in which 4,4'-bpy ligands coordinate with Cd(II) ions along the crystallographic b-axis. **PCP-6** has channels (Figure 6.5. (b)) with diameters of approximately $4.7 \times 9.99 \text{ \AA}^2$ and the overall accessible volume for **PCP-4**, after removing guest molecules, is 27.3%.

6.4. Powder X-ray Diffraction and Thermal Properties

PXRD patterns were employed to assess the phase purity of the synthesized PCPs, consistently indicating their formation as single-phase structures with slight variations in peak intensities (Figure 6.6). In light of conducting photocatalytic degradation experiments in an aqueous medium, it was crucial to evaluate the water stability of the synthesized compounds. Post-photocatalytic experiments, PXRD patterns of **PCP-3-6** confirmed their chemical stability (Figure 6.6. 2 (a-d)), underscoring the resilience of the PCPs crystal lattice under photocatalytic conditions. The PXRD patterns after exposure to UVA light closely matched those of the as-synthesized compounds, providing evidence of the PCPs' photocatalytic stability.

The thermal stability of the synthesized PCPs and the ligand H₆L was evaluated through TGA. TGA curves demonstrated that the degradation of H₆L began at 301 °C. TGA measurements, performed under airflow

With a heating rate of 10 °C/min (Figure 5.6), revealed the liberation of crystal H₂O, along with DMF, DEF, formate anions, and dimethyl amine cations in PCPs within the temperature range of 30 to 200 °C.

In the TGA of **PCP-3**, an initial 10% weight loss occurs between 25–160 °C, indicating the removal of lattice molecules such as aqua, DMF molecules, formate anions, and dimethyl amine cations per formula unit. The desolvated **PCP-3** remains stable up to 350 °C before undergoing decomposition, accompanied by the loss of organic ligands. For coordination polymer **PCP-4**, a gradual 8% weight loss is observed in the range of 25–155 °C, attributed to the release of aqua and DEF molecules per formula unit. Desolvated **PCP-4** exhibits stability within the temperature range of 170–370 °C, followed by decomposition.

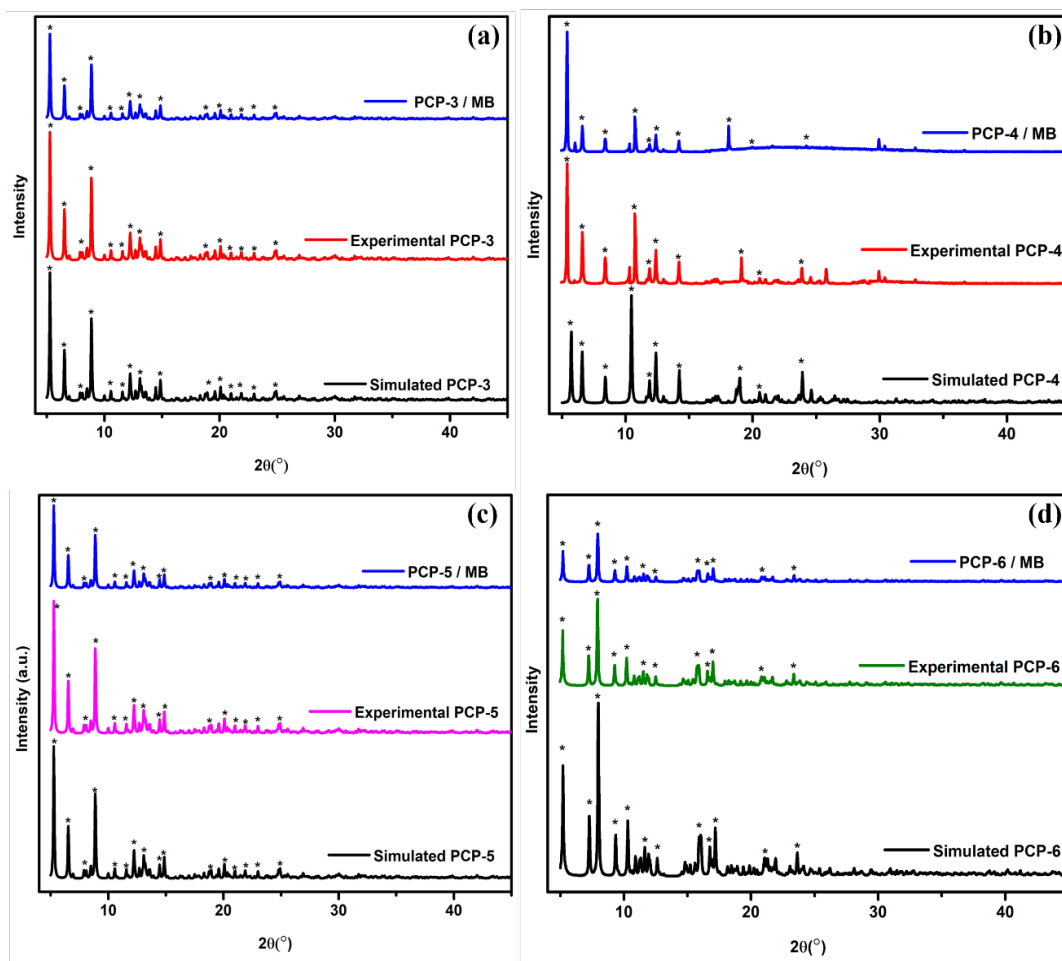


Figure 6.6: PXRD patterns of the simulated, experimental and after photocatalytic MB dye removal of PCPs. (a) **PCP-3**, (b) **PCP-4**, (c) **PCP-5**, (d) **PCP-6**.

In the TG curve of **PCP-5**, an initial 8% weight loss occurs between 25–150 °C, signifying the removal of lattice molecules, specifically aqua and DMF molecules per formula unit. Desolvated **PCP-5** remains stable up to 350 °C before undergoing decomposition, accompanied by the loss of organic ligands.

As for coordination polymer **PCP-6**, a gradual 15% weight loss is observed in the range of 25–158 °C, attributed to the release of aqua and DEF molecules per formula unit. Desolvated **PCP-6** exhibits stability within the temperature range of 160–360 °C, followed by decomposition. The observed weight losses in the specified temperature ranges suggest the removal of solvent molecules from the CPs. The stability of the desolvated forms in distinct temperature ranges indicates their resistance to thermal decomposition up to certain temperatures. Beyond these stable temperature ranges, the CPs undergo decomposition, marked by the loss of organic ligands. Understanding the thermal stability of these CPs is crucial for applications where thermal conditions play a significant role, such as in catalysis or as components in advanced materials.

PCP-4 and **PCP-6** show enhanced thermal stability compared to **PCP-3** and **PCP-5**. **PCP-4** and **PCP-6** exhibit decomposition at higher temperatures compared to **PCP-3** and **PCP-5**. The differences in thermal stability could be attributed to the specific structures and compositions of the **PCP-4** and **PCP-6** appear to have superior thermal stability compared to **PCP-3** and **PCP-5**. The nature of the released molecules during weight loss and the specific structural features likely contribute to the observed differences in thermal behavior. Understanding these thermal characteristics is crucial for tailoring CPs for applications requiring stability under varying temperature conditions, such as in catalysis or as components in advanced materials. The enhanced thermostability of **PCP-4** compared to **PCP-3** is attributed to the stacking structure of **1** as opposed to the porous structure of **2**. Examining the TGA curves indicated that the onset of decomposition occurred at 425 °C for **PCP-3**, 388 °C for **PCP-4**, 430 °C for **PCP-5**, 462 °C for **PCP-6**. The organic ligands within the compounds underwent exothermic combustion, resulting in the potential formation of CdO as the final product at 800 °C.

6.5. Optical and Photoluminescence Properties

The semiconductive characteristics of the synthesized compounds depend on their band gaps (E_g), determined through UV/vis diffuse reflectance measurements (UV-DRS). In evaluating photocatalytic properties, the optical band gap (E_g) is crucial, with improved efficiency often linked to a narrower energy gap between the valence and conduction bands. The Kubelka-Munk (K-M) function, a mathematical tool calculating $F(R)$ (closely tied to the absorption coefficient α), plays a vital role. The absorption coefficient relies on diffuse reflectance (R) and scattering coefficient (S) values. The band gap is determined using the $(\alpha h\nu)^2 \sim h\nu$ curve, where the point of intersection between the tangent line at the linear absorption edge and the $y = 0$ axis is crucial. Figure 6.1 (a-d) illustrates band gap measurements of 3.93 eV for **PCP-3**, 3.61 eV for **PCP-4**, 3.40 eV for **PCP-5**, and 3.67 eV for **PCP-6**. The K-M function is represented as given in Equation 2.

$$F(R) = \frac{(1-R)^2}{2R} = \frac{\alpha}{S} \quad (6.1)$$

PCPs with Cd(II) centers exhibit photoluminescent properties. The fluorescence of **PCP-3**, **PCP-4**, **PCP-5**, **PCP-6**, and H_6L was examined in the solid state at room temperature with excitations at 320, 335, 280, 300 and 280 nm, respectively (refer to Figure 6.7.).

The unbound ligand exhibit pronounced emission peaks at 301 and 311 nm ($\lambda_{ex}H_6L = 260$ nm), likely originating from both $\pi-\pi^*$ and $n-\pi^*$ transitions. These emissions of the free ligand can be attributed to intraligand transitions, including $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$. The emission spectrum of **PCP-3** displays two robust peaks at 363 and 376 nm ($\lambda_{ex} = 320$ nm), indicating σ -donation from the Cd(II) centers, suggestive of LMCT phenomena. Similarly, **PCP-4** exhibits two intense peaks at 361 and 378 nm ($\lambda_{ex} = 335$ nm), also attributed to ligand-to-metal charge transfer (LMCT). The emission spectrum of **PCP-5** displays two robust peaks at 362 and 378 nm ($\lambda_{ex} = 280$ nm), indicating σ -donation from the Cd(II) centers, suggestive of LMCT phenomena. Similarly, **PCP-6** exhibits two intense peaks at 379 and 387 nm ($\lambda_{ex} = 300$ nm), also attributed to LMCT.

Compared to the emission band of the free H₆L ligand, **PCP-3**, **PCP-4**, **PCP-5** and **PCP-6** exhibited slight red shifts. These shifts in the emission spectra of the PCPs can be influenced by various factors, including coordination behavior, enhanced structural rigidity of ligands, and the robustness of the framework.

The variation in emission peak positions may be attributed to differing coordination environments and modes surrounding the cadmium ions in **PCP-3**, **PCP-4**, **PCP-5**, **PCP-6**. This difference in photoluminescent behavior underscores the intimate connection between the metal ions and the ligands coordinated to the metal centers.

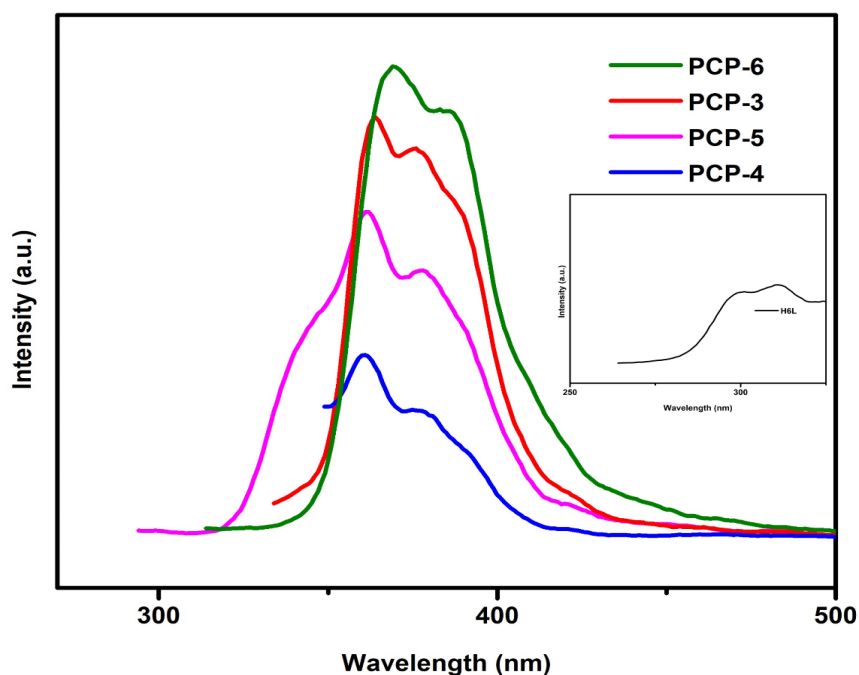


Figure 6.7: The solid-state emission spectra of the ligand H₆L and PCPs at room temperature.

6.6. Photocatalytic Properties

Photocatalysis emerges as a promising strategy for mitigating textile industry wastewater pollution by degradation of organic dyes. This study investigates the photocatalytic degradation of model dyes (MB, RhB, MO, and RO16) in aqueous solutions using CPs as photocatalysts. Control experiments were conducted to evaluate dye degradation in the absence of photocatalysts.

The calculated band gap values for **PCP-3**, **PCP-4**, **PCP-5**, **PCP-6** were 3.93, 3.61, 3.40 and 3.67 eV respectively, placing them in the semiconductor range and indicating their suitability for conducting photocatalytic experiments. UV irradiation with a UVA lamp was employed during the photocatalytic experiments. Figures 6.8 – 6.11 showcases the remarkable photocatalytic performance of **PCP-3-6** achieving degradation efficiencies above 90% for dyes MB, RhB, MO, and RO16. However, variations were observed in their efficiencies and kinetics. Introducing a photocatalyst composed of CPs (300 mg/L) into a 20 ppm, 100 mL dye solution, the decomposition was monitored by assessing distinctive absorption bands. In the absence of illumination, **PCP-3-6** showed negligible changes in the absorption bands of the dyes.

Table 6.3: The pseudo first-order rate constants k (min^{-1}) and the corresponding square of the correlation coefficients R^2 data for the photocatalytic degradation reactions of MB, RhB, MO and RO16 catalyzed by PCPs.

	MB	RhB	MO	RO16
PCP-3	0,0816 (0,9544)	0,0375 (0,9859)	0,0321 (0,9931)	0,0318 (0,9859)
PCP-4	0,0709 (0,9678)	0,0356 (0,9780)	0,0475 (0,9817)	0,0372 (0,9832)
PCP-5	0,0656 (0,9411)	0,0325 (0,9806)	0,0418 (0,9827)	0,0345 (0,9827)
PCP-6	0,0623 (0,9334)	0,0299 (0,9710)	0,0362 (0,9956)	0,0326 (0,9875)

Figures 6.8. – 6.11. depict concentration ratios ($\ln C_0/C$) of MO, MB, and RhB over irradiation time with PCPs as photocatalysts, and kinetics plots are presented in Figure 6.8 – 6.11. Associated rate constants (k) and R^2 parameters are compiled in Table 6.3. Photocatalytic degradation efficiencies and kinetic constants (k , min^{-1}), fitted with the pseudo-first-order rate equation, are summarized as follows:

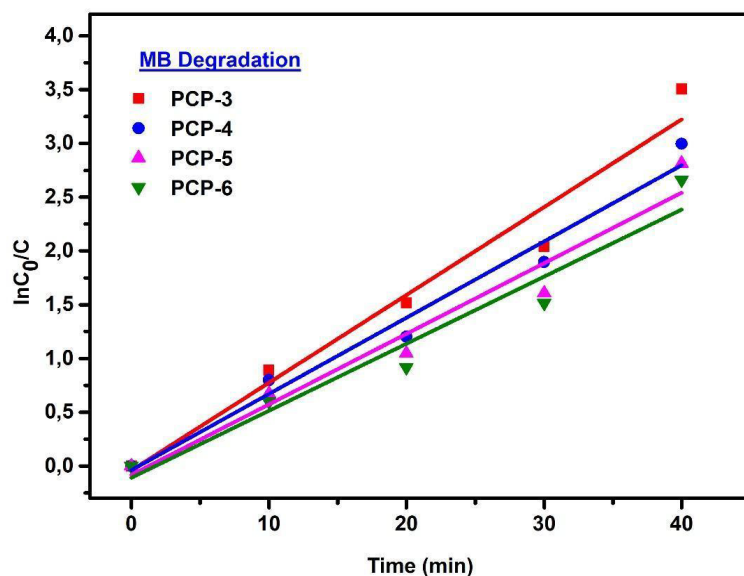


Figure 6.8: The pseudo first-order plots for the photodegradation of MB under UVA irradiation in the presence of PCPs.

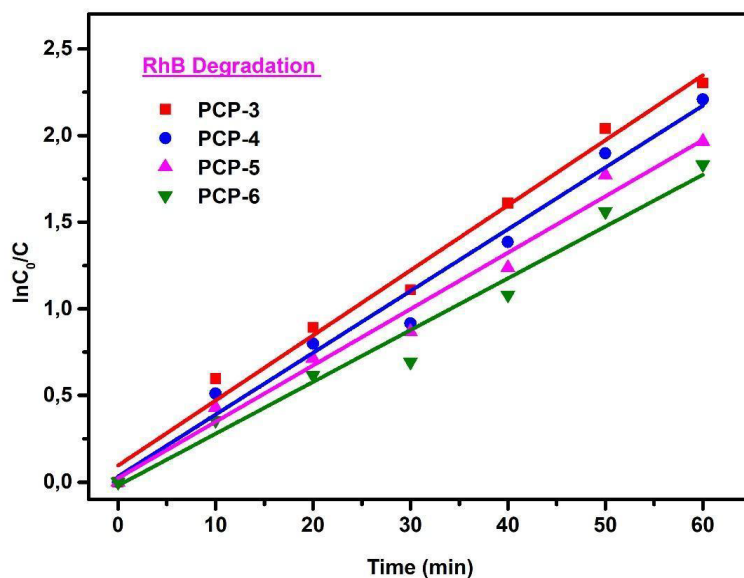


Figure 6.9: The pseudo first-order plots for the photodegradation of RhB under UVA irradiation in the presence of PCPs.

For MB degradation within 40 minutes: **PCP-3** (97%, 0.0816) > **PCP-4** (95%, 0.0709) > **PCP-5** (94%, 0.0656) > **PCP-6** (93%, 0.0623).

For RhB degradation within 60 minutes: **PCP-3** (90%, 0.0375) > **PCP-4** (89%, 0.0356) > **PCP-5** (86%, 0.0325) > **PCP-6** (84%, 0.0299).

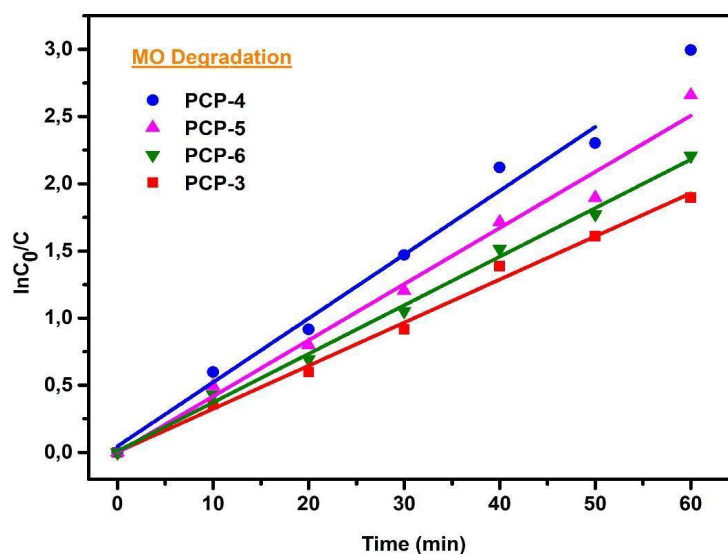


Figure 6.10: The pseudo first-order plots for the photodegradation of MO under UVA irradiation in the presence of PCPs.

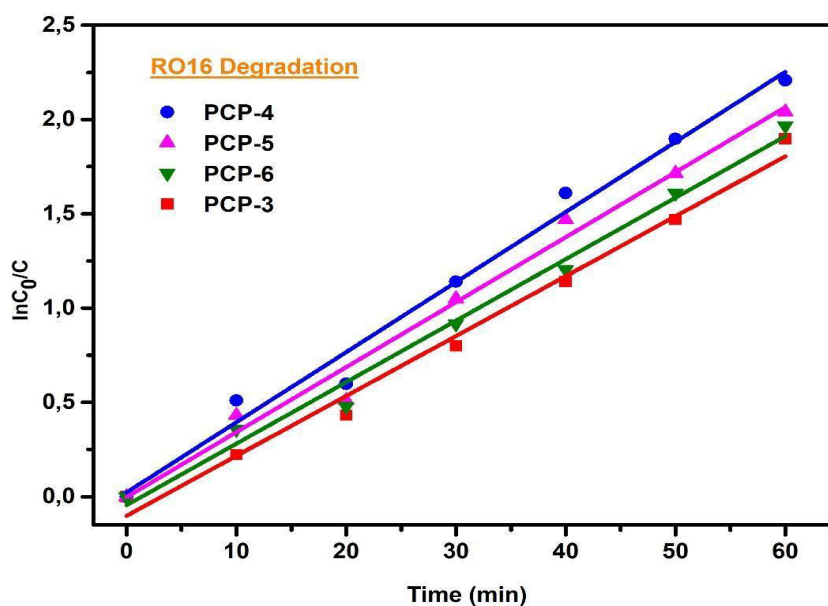


Figure 6.11: The pseudo first-order plots for the photodegradation of RO16 under UVA irradiation in the presence of PCPs.

For MO degradation within 60 minutes: **PCP-4** (95%, 0.0475) > **PCP-5** (93%, 0.0418) > **PCP-6** (89%, 0.0362) **PCP-3** > (85%, 0.0321).

For RO16 degradation within 60 minutes: **PCP-4** (89%, 0.0372) **PCP-5** (87%, 0.0345) > **PCP-6** (86%, 0.0326) > **PCP-3** (85%, 0.0318).

On the contrary, in experiments conducted without photocatalysts, the degradation efficiencies of 20 ppm dye solutions increased to 8% within 40 minutes for MB and 9% within 60 minutes for RhB, MO, and RO16. The investigation systematically explored the dye degradation kinetics of Cd(II) CPs, namely **PCP-3**, **PCP-4**, **PCP-5**, and **PCP-6**, concerning four different organic dyes: MB, RhB, MO, and RO16. The study quantified the efficiency of dye degradation within specific time intervals, revealing distinct trends in the degradation performance of **PCP-3** to **PCP-6**.

MB Degradation: Over 40 minutes, **PCP-3** demonstrated superior performance in MB degradation, achieving an impressive 97% degradation with a rate constant of 0.0816. **RhB Degradation:** In the case of RhB degradation within 60 minutes, **PCP-3** once again displayed enhanced performance, achieving a notable 90% degradation, accompanied by a degradation rate constant of 0.0375. **MO Degradation:** **PCP-4** exhibited superior capability in the degradation of MO within 95 minutes, achieving an impressive 95% degradation with a rate constant of 0.0475.

RO16 Degradation: Similar trends were observed in the degradation of RO16 within 60 minutes, with **PCP-4** outperforming and achieving a degradation efficiency of 89%, along with a rate constant of 0.0372.

The trends in dye degradation kinetics indicate that specific ligand modifications in PCPs play a crucial role in enhancing the photocatalytic activity of Cd(II) CPs. The higher degradation percentages and rate constants for **PCP-3** and **PCP-4** compared to **PCP-5** and **PCP-6** across all tested dyes suggest improved efficiency in removing organic dyes from aqueous solutions.

The enhanced performance of **PCP-3** and **PCP-4** can be attributed to modified ligands, facilitating more effective electron transfer and reactive species generation during the photocatalytic process. The unique molecular structures of the ligands in **PCP-3** and **PCP-4** likely contribute to increased surface area, improved light absorption, and optimized catalytic sites, resulting in superior dye degradation performance.

These findings underscore the significance of ligand engineering in tailoring the properties of CPs for efficient photocatalytic applications. Further exploration of the underlying molecular mechanisms and structural characteristics of **PCP-3** and **PCP-4**

could provide valuable insights for designing advanced materials with enhanced photocatalytic performance in environmental remediation processes.

The investigation aimed to assess the viability of reusing photocatalysts PCPs in catalytic processes across multiple cycles. Each experiment employed freshly prepared dye solutions under optimal conditions, featuring a catalyst concentration of 300 mg/L, a dye concentration of 20 mg/L, pH 5.2, and a temperature of 25°C. Post-experiment, the catalyst underwent filtration, deionized water washing, and overnight drying at 50°C.

Although there was a modest decrease in catalytic efficiency across consecutive cycles, the approach demonstrated both environmental sustainability and economic feasibility. Notably, **PCP-3** witnessed a decline from 97% to 80%, **PCP-4** decreased from 95% to 86%, **PCP-5** experienced a decline from 94% to 85%, and **PCP-6** dropped from 93% to 85% by the 5th cycle, as depicted in Figure 6.12 (a - d). This slight reduction in performance was linked to the degradation of catalytic sites.

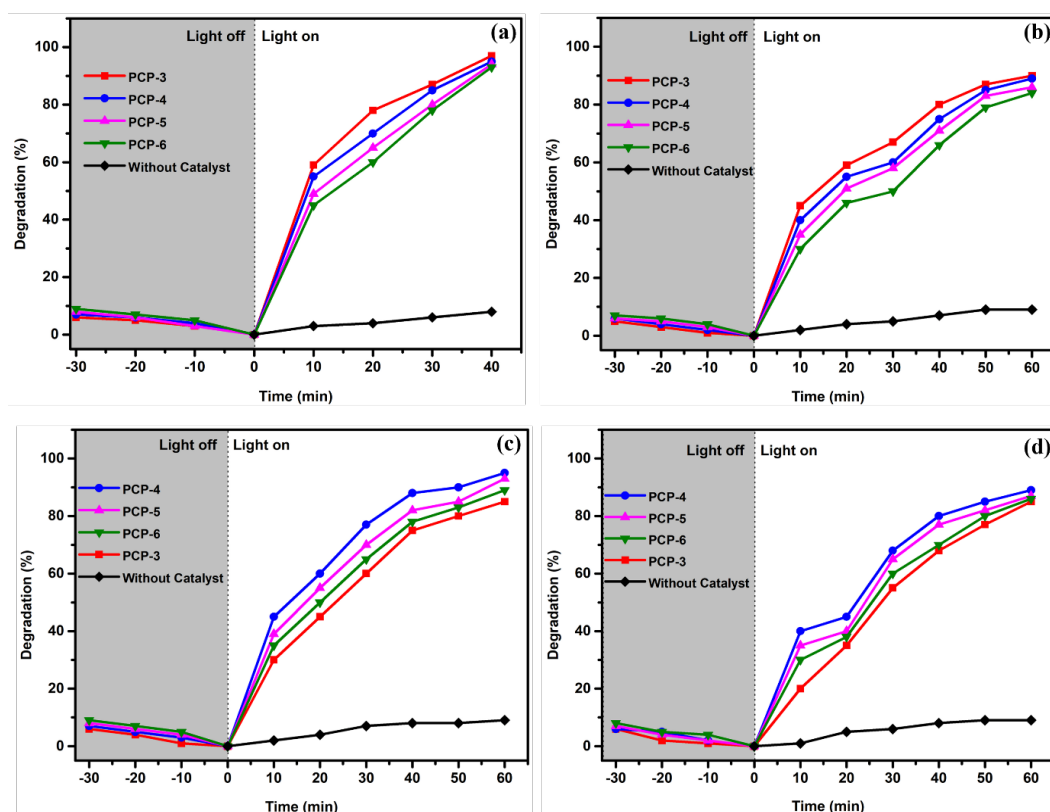


Figure 6.12: Photodegradation of MB (a), RhB (b), MO (c) and RO16 (d) in the presence of PCPs.

The study highlights a reduction in the effectiveness of removing MB dye after five cycles, underscoring the need for a more in-depth exploration of surface interactions. Nonetheless, the current approach holds promise for repetitive use in water restoration initiatives. The demonstrated reusability of these photocatalysts not only emphasizes their significance but also enhances their relevance in the field of water remediation. This highlights their potential for repetitive utilization in addressing water pollution concerns, showcasing both environmental sustainability and practical applicability in water restoration endeavors [17,18].

In analyzing the information provided above, the stability of the catalysts can be assessed through their performance across multiple cycles in catalytic processes. The slight decrease in efficiency is attributed to the degradation of catalytic sites. Despite this decline, the methodology showcases both environmental sustainability and economic feasibility, indicating that the catalysts maintained a reasonably high level of stability over several cycles. The study underscores the practical applicability of these catalysts in water restoration efforts, despite a modest reduction in catalytic efficiency. Further exploration of surface interactions and regeneration techniques could contribute to enhancing their stability and extending their usability in future applications.

Photocatalytic dye degradation represents an intricate process involving the interaction of light-activated catalysts with organic dyes. Within this mechanism, scavengers assume a pivotal role in mitigating undesired side reactions and elevating the efficiency of the degradation process. In our exploration of the intricate photocatalytic mechanism governing the degradation of organic dyes in Cd (II) CPs, we emphasize the crucial function of scavengers in refining both the efficiency and selectivity of the process. Our focus extends to three specific scavengers—BQ, IPA) and EDTA—and their distinct mechanisms in the context of photocatalytic degradation.

Benzoquinone, acting as a $O_2^{\bullet-}$ scavenger, intercepts $O_2^{\bullet-}$ radicals, forming stable adducts that effectively quench their reactivity. This scavenging action is instrumental in preventing unwanted side reactions associated with $O_2^{\bullet-}$. $O_2^{\bullet-}$ radicals, ultimately enhancing the overall photocatalytic efficiency. Expanding beyond Benzoquinone, additional scavengers like IPA and EDTA further contribute to fine-tuning the photocatalytic mechanism. IPA functioning as a $\bullet OH$ scavenger, intercepts reactive

•OH, thereby mitigating their impact on the degradation process. Meanwhile, EDTA, as a metal chelator, complexes with metal ions that might inadvertently partake in undesired side reactions, thereby enhancing the selectivity of the photocatalytic degradation.

In our investigation of the photocatalytic and photoluminescent properties of Cd(II) CPs, crafted from a unique combination of a cyclotriphosphazene ligand adorned with hexacarboxyl functionalities, and phen, trp, 2,2'-bpy and 4,4'-bpy ligands the photocatalytic dye degradation mechanism emerges as a crucial focus. This process involves the generation of e^-/h^+ pairs upon exposure to light. However, the simultaneous formation of O_2^- quenching. O_2^- during these reactions can impede overall efficiency and lead to undesired side reactions. To address this challenge, we introduce Benzoquinone as a $O_2^{\bullet-}$ scavenger, playing a vital role in quenching. $O_2^{\bullet-}$ radicals, forming stable adducts, and mitigating their potential interference in the dye degradation process. The incorporation of Benzoquinone as a scavenger not only enhances the efficiency of photocatalytic degradation but also enables a more controlled and optimized reaction pathway.

Measurements conducted in the presence of 1 μ M p-benzoquinone suggest a marginal enhancement in the dye degradation rate. Conversely, the investigation into the impact of p-benzoquinone reveals a significant role played by $\bullet O_2^-$ ($O_2^{\bullet-}$) for **PCP-4** and **PCP-5** as depicted in Figure 6.14. The presented findings strongly indicate that $O_2^{\bullet-}$. $\bullet O_2^-$ serve as the predominant reactive species governing the degradation of MB dye (Figure 6.13).

Experiments carried out with 1 μ M IPA indicate a slight improvement in the dye degradation rate. In contrast, the analysis of the influence of p-benzoquinone unveils a notable involvement of •OH. OH for **PCP-3** and **PCP-6**, as illustrated in Figure 6.14. These results strongly suggest that •OH.OH play a pivotal role as the primary reactive species governing the degradation of MB dye. The photocatalytic mechanism of all dyes and PCPs was investigated, and the details are presented in Figure 6.14 – 6.17.

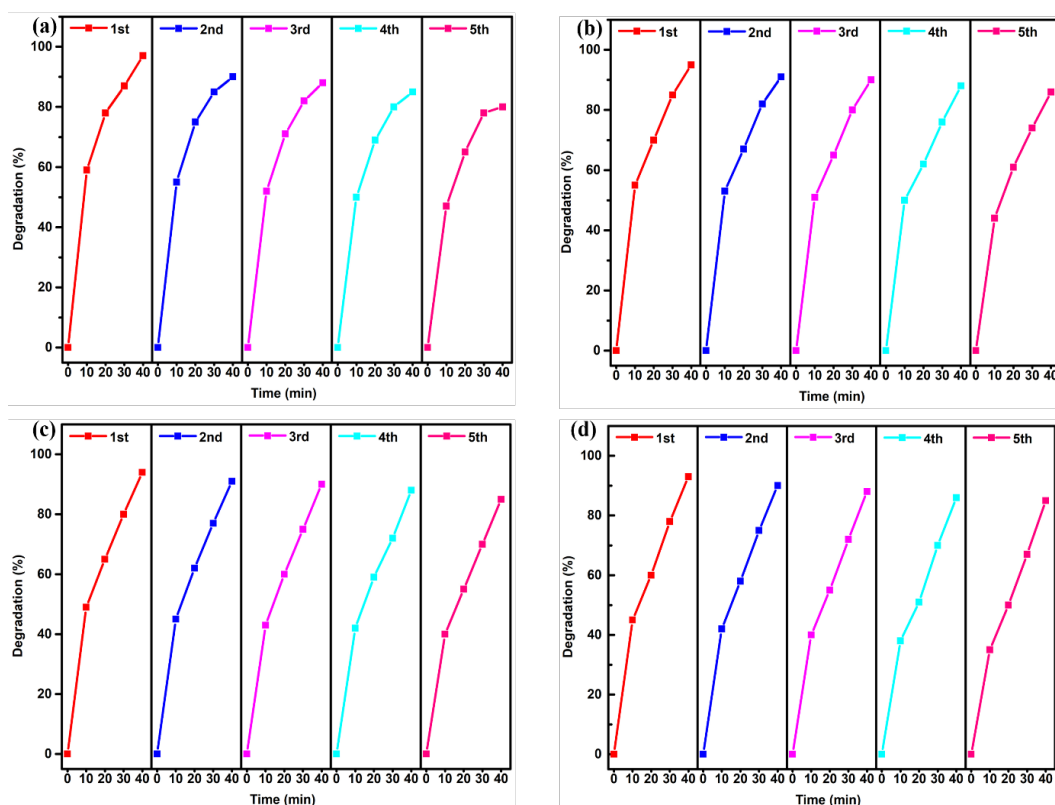


Figure 6.13: Reuse of catalyst PCPs for photocatalytic decolorization of MB dye. (a) PCP-3, (b) PCP-4, (c) PCP-5, (d) PCP-6.

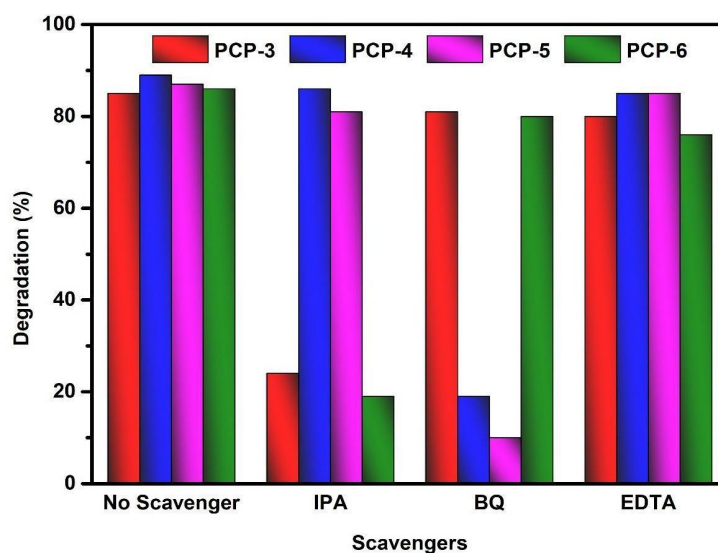


Figure 6.14: Photocatalytic degradation of RhB by PCPs in the presence of scavengers.

Illustrative diagram as shown in Figure 6.14 – 6.17 demonstrates how the inclusion of specific scavengers influences the mechanism of MB degradation.

This comprehensive approach to understanding the photocatalytic and photoluminescent properties of our Cd(II) CPs underscores the critical role of scavengers in fine-tuning and optimizing the performance of these materials. Such explorations are essential for advancing the application of these CPs in environmentally relevant processes and technologies. [19,20].

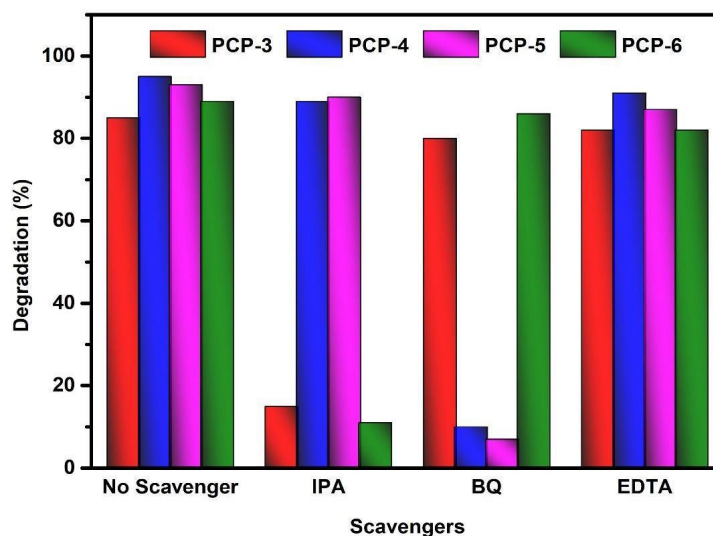


Figure 6.15: Photocatalytic degradation of MO by PCPs in the presence of scavengers.

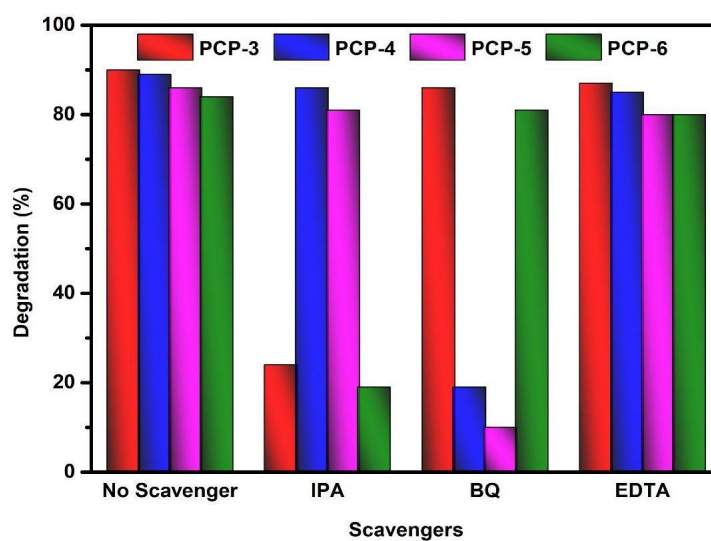


Figure 6.16: Photocatalytic degradation of RO16 by PCPs in the presence of scavengers.

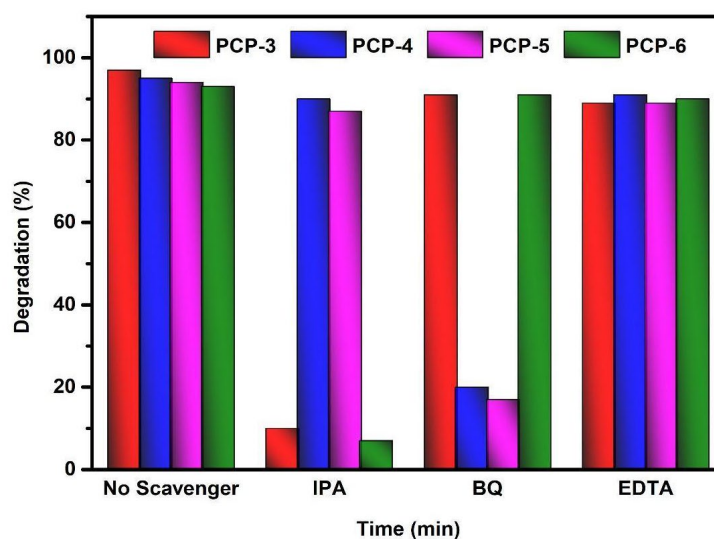


Figure 6.17: Photocatalytic degradation of MB by PCPs in the presence of scavengers at the end of the 45 min experiment as a function of scavengers.

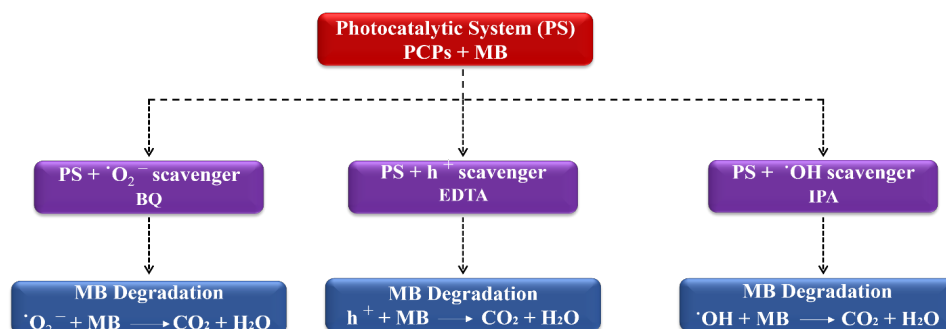


Figure 6.18: Schematic diagram showing the effect of the inclusion of specific scavengers on the mechanism of MB degradation.

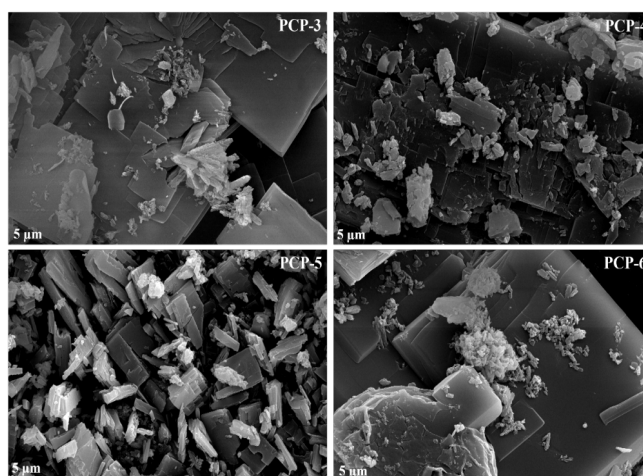


Figure 6.19: SEM images of PCP-3, PCP-4, PCP-5, PCP-6: before UVA irradiation (a) PCP-3, (b) PCP-4, (c) PCP-5, (d) PCP-6.

7. CONCLUSION

In conclusion, this study four novel cyclotriphosphazene-based Cd(II) CPs employing N-donor ligands and a hexacarboxylic acid moiety were successfully synthesized and characterized. PCPs demonstrated remarkable photocatalytic activities in the degradation of MB, RhB, MO, and RO16 dyes from aqueous solutions, achieving notable efficiencies of up to 95% degradation within 40 to 60 minutes. The photocatalytic efficacy of PCPs was attributed to their unique combination of porosity, rigidity, chemical stability, and flexibility, underscoring the significant role of electrostatic interactions in the photocatalytic process. This study highlights the potential of these CPs as effective photocatalysts for dye removal in wastewater treatment, marking a pioneering example of cyclotriphosphazene-based CPs with N-donor modifications and dye degradation properties. Additionally, the flexible CPs demonstrated exceptional reusability and efficiency over five consecutive runs. The elucidation of the photocatalytic degradation mechanism identified O_2^- and $\cdot OH$ as the primary reactive radicals involved in the process. In summary, the synthesized cadmium(II) based CPs, ranging from 1D tubular structure to 3D porous frameworks, exhibit promising photocatalytic activities dependent on the N-donor type, positioning them as potential key photocatalysts for future research in the field.

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BIOGRAPHY

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