DEVELOPMENT OF METAL-FREE ORGANIC PHOTOCATALYST FOR ENVIRONMENTAL REMEDITION

M.Sc. Thesis

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DISCIPLINE OFCHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE

JUNE, 2020

DEVELOPMENT OF METAL-FREE ORGANIC PHOTOCATALYST FOR ENVIRONMENTAL REMEDITION

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of Master of Science

> by NIKITA



DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE, 2020



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **DEVELOPMENT OF METAL-FREE ORGANIC PHOTOCATALYST FOR ENVIRONMENTAL REMEDITION** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DISCIPLINE OF CHEMISTRY**, **Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July 2019 to June 2020 under the supervision of **Dr. Apurba K. Das**, Associate Professor, Discipline of Chemistry, Indian Institute of Technology Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

NIKITA

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ACKNOWLEDGEMENTS

I would like to express gratitude towards project supervisor **Dr. Apurba K. Das** (Associate Professor, Discipline of Chemistry, Indian Institute of Technology Indore) for permitting me to work in the field of my interest with his research group. His most valuable guidance and advice, along with motivational support throughout the project work, helped to complete project work.

I would also like to thank **Dr. Anjan Chakraborty** and **Dr. Tushar Kanti Mukherjee** for their precious suggestions and guidance.

I also wish to thank **Prof. Neelesh Kumar Jain**, Director, Indian Institute of Technology Indore, for his constants encouragement and support in every manner.

I would like to thank all of the faculty members of the Discipline of Chemistry for their motivational inspiration.

I would also like to thank all of the lab-mates for their valuable suggestions and constant help.

I would like to thank the Discipline of Chemistry, IIT Indore for allowing me to work in the laboratory.

I am also thankful to SIC, IIT Indore and its member for their technical help and support.

I am also thankful to all my friends, who helped directly-indirectly during post-graduation program.

I would also like to express the deepest gratitude to my family and friends for their kind cooperation, understanding, and valuable support.

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Dedicated to My Family

Abstract

Self-assembled covalent organic polymers (COPs) have gained significant attention in diverse applications. Orienting from nanoscale morphology with high surface area and lower band gap COPs arise as an efficient catalytic material for various redox transformations. The polydiacetylene (PDA) based COPs (PDA-COPs) show optical and electronic properties. In this study, 1,3-diacetylene symmetric monomer covalently linked with biomolecules like phenylalanine and adenine i.e. F-DA-F and A-DA-A have been synthesized. Due to various interactions like hydrogen bonding, π - π and hydrophobic interactions, F-DA-F self-assembles to form the supramolecular nanofibrous network and undergoes polymerization under UV irradiation (15 minutes, 254 nm) to form conjugated polydiacetylene functionalized covalent organic polymer (PDA-F-COP). The monomer of A-DA-A undergoes polymerization under UV irradiation to form PDA-A-COP. The resulting metal-free PDA-F-COP shows efficient catalytic properties under UV irradiation for dye degradation.

TABLE OF CONTENTS

LIST OF FIGURES	xi-xii
LIST OF TABLES	xiii
NOMENCLATURE	xiv
ACRONYMS	xv-xvi
Chapter 1: Introduction	1-4
1.1 Introduction	1-2
1.2 Synthetic scheme	3-4
Chapter 2: Experimental section	5-9
2.1 Materials	5
2.2 General characterization	5
2.3 Synthesis of diacetylene-based monomers	5-9
2.3.1 Synthesis of methyl ester of L-phenylalanine (2)	5-6
2.3.2 Synthesis of 4	6
2.3.3 Synthesis of 5	6-7
2.3.4 Synthesis of 6	7
2.3.5 Synthesis of 8	8
2.3.6 Synthesis of 11	8-9
2.3.7 Synthesis of 12	9
2.4 Photopolymerization experiment	9
Chapter 3: Results and Discussion	10-20
3.1 Gelation study	10-11
3.2 Rheological properties of the gel	11-12
3.3 Photopolymerization Experiment	12-13
3.4 UV-Vis spectroscopy analysis	13-14

APPENDIX-A	21-29
Chapter 4: Conclusion	20
3.9 Photocatalytic performance of PDA-F-COP	18-19
3.8Electrochemical properties of PDA-F-COP	17-18
3.7 Morphological analysis	16
3.6 Structural analysis	15-16
3.5 Raman Spectroscopic analysis	14-15

REFERENCES	30-35

LIST OF FIGURES

Figure 1.Organogel of F-DA-F monomer in toluene.and dynamic frequency sweep of toluene gel of F-DA-F.

Figure 2. (a) Schematic mechanism of photopolymerization, (b) solid state photopolymerization of F-DA-F and (c) solid state photopolymerization of A-DA-A.

Figure 3.UV-Vis absorbance spectra of F-DA-F and PDA-F-COF.

Figure 4.Raman spectrum of F-DA-F and PDA-F-COP.

Figure 5. Wide angle PXRD spectra of the F-DA-F before and after UV light irradiation.

Figure 6. SEM images of (a) F-DA-F and (b) PDA-F-COP.

Figure 7.Cyclic voltammograms of (a) F-DA-F monomer and (b) PDA-F-COF.

Figure 8.Photocatalytic disintegration of Rhodamine B dye in (a) presence of

PDA-F-COP and (b) absence of PDA-F-COP under UV-Vis light.

Figure 9.Schematic diagram of probable mechanism for dye degradation using PDA-F-COP photocatalyst.

Figure 10.¹H NMR (400 MHz, CDCl₃) spectrum of compound 4.
Figure 11.¹³C NMR (100 MHz, CDCl₃) spectrum of compound 4.
Figure 12.¹H NMR (400 MHz, CDCl₃) spectrum of compound 5.
Figure 13.¹³C NMR (100 MHz, CDCl₃) spectrum of compound 5.
Figure 14.¹H NMR (400 MHz, DMSO-*d*6) spectrum of compound 6.
Figure 15.¹³C NMR (100 MHz, DMSO-*d*6) spectrum of compound 6.
Figure 16.¹H NMR (400 MHz, DMSO-*d*6) spectrum of compound 8.
Figure 17.¹³C NMR (100 MHz, DMSO-*d*6) spectrum of compound 8.
Figure 18.¹H NMR (400 MHz, DMSO-*d*6) spectrum of compound 11.
Figure 19.¹³C NMR (100 MHz, DMSO-*d*6) spectrum of compound 11.
Figure 20.¹H NMR (400 MHz, DMSO-*d*6) spectrum of compound 11.
Figure 20.¹H NMR (400 MHz, DMSO-*d*6) spectrum of compound 11.
Figure 20.¹H NMR (400 MHz, DMSO-*d*6) spectrum of compound 11.
Figure 20.¹H NMR (400 MHz, DMSO-*d*6) spectrum of compound 11.
Figure 20.¹H NMR (400 MHz, DMSO-*d*6) spectrum of compound 12.
Figure 21.ESI-MS spectrum of compound 5.
Figure 23.ESI-MS spectrum of compound 5.
Figure 23.ESI-MS spectrum of compound 6.

Figure 24.ESI-MS spectrum of compound 8.

Figure 25.ESI-MS spectrum of compound 11. Figure 26.ESI-MS spectrum of 12.

LIST OF TABLES

Table 1.Gelation study of F-DA-F.

NOMENCLATURE

nm	Nanometre
δ	Delta
mmol	Milimol
μΜ	Micro molar
mL	Millilitre
mg	Milligram
g	Gram
λ	Lambda

ACRONYMS

Abbreviations used for compounds, substituents, reagents, etc. are mainly by the recommendations of the IUPAC. Additional abbreviations used in this thesis are listed below.

F	Phenylalanine
F-OMe	Phenylalanine methyl ester
CDCl ₃	Chloroform-d
DMSO-d6	Dimethyl Sulfoxide-d6
DMF	N, N'-Dimethylformamide
HCl	Hydrochloric acid
Na ₂ CO ₃	Sodium Carbonate
aq.	Aqueous
d	Doublets
ESI-MS	Electron Ionization Mass
	Spectrometry
NaOH	Sodium Hydroxide
MeOH	Methanol
NMR	Nuclear Magnetic Resonance
S	Singlet
min.	Minute
SOCl ₂	Thionylchloride
TLC	Thin Layer Chromatography
t	Triplet
UV-Vis	Ultra violet-visible
ACN	Acetonitrile
DCC	Diisopropylcarbodiimide
m	Multiplet
THF	Tetrahydrofuran
HOBt	N-Hydroxybenzotriazole
Na ₂ SO ₄	Sodium sulphate

1-(3-dimethylaminopropyl)-3-
ethylcarbodiimide hydrochloride
4-dimethylaminopyridine
Round bottom flask
Dichloromethane
Ethyl Acetate
Tetrabutylammoniumhexafluoroph
-osphate

Chapter 1

Introduction

1.1 Introduction

Nowadays, synthetic dyes are more prevalent than naturally available dyes due to their long term stability with increasing demand and high economic feasibility.^{[1][2]} However, the extensive use of synthetic dyes is proven to get bioaccumulated in aquatic fauna and thereby get transferred to the higher food chain, which results in possible health ailments of the consumers.^[2] The high visibility of synthetic dyes even at low concentration adversely affects the photosynthetic activities of aquatic plant and algae and thereby causes a reduction in dissolved oxygen and as a result, harming aquatic life.^[2] The development of effective ways to extract and degrade pollutant dyes from the environment has gained significant attention of worldwide researchers.^{[3][4][5][6][7]} The persistent behavior of synthetic dyes in water leads to water pollution, which gives birth to severe major environmental disorders which are a threat to human health and sustainable development. The use of chemical oxidation and reduction using several oxidation and reduction agents is feasible in economic ways for the removal of highly concentrated pollutants.^[8] From the last decades, many efforts in the research were employed to develop semiconductor-based material which could be used for photocatalytic degradation of synthetic dye pollutants prevailed in the environment.^{[9][10]} The photocatalysts catalyze various oxidation and reduction process under the irradiation of UV and visible light which results in mineralization of non-degradable dye pollutant.^[11] The high rate of catalyst recovery and reusability of heterogeneous catalysts made them as a promising candidate for aquatic dye degradation.^[12]

The porous organic material and derivatives such as covalent organic polymers (COPs),^[13] covalent organic frameworks (COFs),^{[14][15]} metal-organic frameworks^[16] and organic-inorganic nanohybrids have gained attention as an active material for several applications including drug delivery,^{[17][18]} gas sensing,^{[19][20]} energy storage and conversion.^[21] Covalent organic polymers

(COPs) hold great potential for diverse applications, including catalysis, sensing, energy conversion and storage.^{[13][22][23][24]}Among various applications, several COPs and derivatives were used as the active material for various photocatalytic applications due to their compatible optical properties.^[25] COPs allow the development of metal-free organic photocatalyst through the introduction of a conjugated network.^[26] Various polymerization techniques have been developed by worldwide researchers to synthesis covalently linked conjugated network of COPs.^{[27][28][29]} The diacetylene based polymers have brought considerable attention in the previous few decades.^[30] Wegner et al. reported the first polydiacetylene (PDA) compound in 1969.^[31] The polydicetylene (PDA) systems have proved to possess various chromatic properties. Their formation is initiated by the irradiation of diacetylene monomers in the UV light, which is not possible in the visible light region.^[32] The intense colored appearance was due to the π - π * transition.^[33] Diacetylenes undergo polymerization when exposed to UV-Vis light at 254 nm by following a topochemical 1,4 addition mechanism.^[34] Diacetylene motifs have the general formula R_1 -C=C-C=C-R_2. Here, C=C-C=C indicates the diacetylene motifs and R₁, R₂ stands for the substituent groups. These motifs polymerize under the required incentive. The polymerization leads to formation of PDA compounds. The linear conjugated polymers with the general formula (= R_{1-} $C=C-R_2=)_n$. The polymerization is accompanied by chromatic change which initiated upon irradiation of γ -rays or UV-light or heat or by the applying pressure on the crystal.^[32] After initiation, 1,4-addition process produces a conjugated eneyne alternated polymer, while the olefins attached to the polymer chain in a trans configuration. In this work, symmetrical biomolecule functionalized monomers of diacetylene were synthesized. The phenylalanine functionalized PDA-F-COP and functionalized adenine PDA-A-COF displayed catalytic properties dye degradation under UV light irradiations. The photocatalytic dye degradation can effectively lead to the reduction in water contamination to some extent, and thereby can contribute to a greener environment.

1.2 Synthetic scheme

Synthesis of phenylalanine linked symmetrical diacetylene-based monomer F-DA-F

Step 1.













Scheme 1.Synthetic scheme of monomer F-DA-F.

Synthesis of adenine linked symmetrical diacetylene based monomer A-DA-A. **Step 1**



Scheme 2.Synthetic scheme of monomer A-DA-A.

Chapter 2

Experimental methods

2.1 Materials

Chemicals including 4-Pentynoic acid, Adenine, copper chloride (I) and N, N, N, N-tetramethylethylenediamine (TMEDA) were bought from Alfa Aesar India. N, N- dicyclohexylcarbodiimide (DCC), L-Phenylalanine, 1-(3-dimethylaminopropyl)-3-ethyl carbodiimidehydrochloride (EDC.HCl), 1-hydroxybenzotriazole (HOBt) and Propargylbromide were purchased by SRL India Pvt. Ltd. Solvents such as DCM, EtOAc, hexane were purchased from Merck India Pvt. Ltd and distilled before use by following procedures of reported literature.

2.2 General Characterization

Mass spectrometry (ESI-MS) was done on a BrukerMicrOTOF-QII operated via electron spray ionization on positive-mode. All NMR spectroscopy was recorded out on a 400 MHz Bruker AV400 NMR. UV–Vis absorbance was recorded at 280 nm. Raman study was carried out on a Micro Raman (400–1100 nm) Jobin Yvon Horiba LABRAM-HR visible system which is equipped with excitation source of Ar⁺ laser (488 nm, 10 mW) and a CCD detector. All of the involved reactions were constantly observed by employing thin-layer chromatography technique (TLC).

2.3 Synthesis of diacetylene-based monomers

2.3.1 Synthesis of methyl ester of L-phenylalanine (2):

In a 100 mL RB flask, methanol (25 mL) was taken and kept for stirring for 15 minutes at 0 °C. The0thionylchloride (SOCl₂) (36.32 mmol, 2.63 mL) was added very slowly with the help of dropping funnel through the walls of the RB flask. L-phenylalanine (18.16 mmol, 3 g) was added to the RB flask, covered with a guard tube. The reaction mixture kept for stirring for overnight at 30 °C. The left over

solvent was evaporated at room temperature by rotary evaporation. Obtained crude compound was washed two times with diethyl ether.

2.3.2. Synthesis of 4:

In a 100 mL RB flask, DMF (dry, 5 mL) was taken and 4-pentynoic acid (5.09 mmol, 0.5 g) was dissolved. The reaction mixture was stirred for 15 minutes in ice-cold condition, followed by addition of DCC (6.10 mmol, 1.23 g). After 5 minutes, HOBt (6.10 mmol, 0.81 g) was added. Methyl ester protected Lphenylalanine was secluded from its analogous methyl ester hydrochloride (10.19 mM, 1.82 g) by neutralization it with a base. After that it was extracted twice by using EtOAc (2 \times 30mL). After that, the organic part was dried over Na₂SO₄ (anhydrous). The solution was concentrated to 4 mL at room temperature by using rotavapour. The resulting solution was then added to their action mixture and the reaction mixture was kept for stirring for 12 hours. After that, the white precipitate of dicyclohexylurea (DCU) was filtered out by using a suction pump. The remaining organic part was then washed with 1 N HCl (3×15 mL), Na₂CO₃ $(3 \times 15 \text{ mL})$ and brine $(3 \times 15 \text{ mL})$. After that, the organic part residue was dried over dry Na₂SO₄ and the solvent was evaporated using rotavapour. Purification of the final compound was done by using flash column chromatography by employing hexane - EtOAc (7:3)as solvent system.

Yield: 90%, 1.19g. ¹H NMR (400 MHz, CDCl₃) δ1.89(1H, s), 2.34(2H, t), 2.43(2H, t), 3.06(2H, m),3.66(3H, s), 4.83(1H, m), 6.03(1H, d), 7.04(2H, m), 7.19(3H, m) ppm.¹³C NMR (400 MHz, CDCl₃) δ172.19, 170.20, 135.94, 129.30, 128.59, 127.31,82.70, 69.40, 53.56, 52.30, 37.87, 35.14, 14.60 ppm.

ESI-MS: m/z calculated for $C_{15}H_{17}NO_3[M+Na]^+$: 282.1208, found282.1151.

2.3.3 Synthesis of 5:

In a 100 mL RB flask, acetone (dry, 10 mL) was taken followed by the addition of CuCl (3.85 mmol, 0.38 g) and TMEDA (3.85 mmol, 0.57 mL). The reaction mixture was kept for stirring for 30 minutes followed by the addition of **4** (1.92mmol, 0.5g). After that, the reaction mixture was kept for stirring in open air

by covering RB flask with cotton swab for 24 hours. The remaining solvent was evaporated using rotary evaporation, followed by the dissolution of the residue in EtOAc. The EtOAc layer was washed using 1 N HCl (2×25 mL) and the solvent was evaporated at vacuum to obtain the crude product. The obtained product was purified by using silica column chromatography using hexane-EtOAc (1:1) as solvent system to yield the compound. The obtained compound was white powder.

Yield: 42%,0.3562g. ¹H NMR (400 MHz, CDCl₃) δ 2.29(4H,t),2.48(4H, t), 3.03(4H, m),3.66, (6H, s), 4.80(2H, m), 6.11(1H,d), 6.30 (1H, d), 7.03(4H, m), 7.20, (6H, m) ppm.¹³CNMR (100 MHz, CDCl₃) δ 172.18, 171.26, 136.00, 129.64, 128.43, 127.11, 76.27, 66.14, 53.10, 52.44, 38.25, 35.02, 15.36ppm. ESI-MS: m/z calculated for C₃₀H₃₂N₂O₆ [M+Na]⁺: 539.2311, found 539.2255.

2.3.4 Synthesis of 6:

In a 100 mL RBflask, compound **5** (1 g) was dissolved in methanol (30 mL),1 N NaOH (2 mL) was added drop wise, and the reaction was continuously observed by employing TLC. The reaction mixture was kept for stirring for 4-5 hours. After the reaction was completed, as indicated by the TLC, the remaining solvent was evaporated at reduced pressure. The organic leftover was then dissolved in water (30 mL). Then the solution obtained was washed by using diethyl ether (2 ×10 mL). After that, the pH of the solution was calibrated to acidic by adding of 1 N HCl. The organic product was then extracted with the help of EtOAc (3× 30 mL).The organic part was dried over Na₂SO₄ (anhydrous) followed by evaporation of EtOAc under vacuum using rotavapour to obtain the analogous carboxylic acid. The product without any further purification was used in next step.

¹H NMR (400 MHz, DMSO-*d*6) δ 2.37(4H, t), 2.54(4H, t), 2.90 (2H,d), 3.10 (2H, d), 4.45, (2H, d), 7.31 (10H), 8.30 (2H, d), 12.70(2H, s) ppm.¹³C NMR (100 MHz, DMSO-*d*6)δ 173.79, 170.47, 138.01, 129.58, 128.56, 126.90, 77.98, 65.95, 53.93, 37.21, 33.90, 15.36 ppm.

ESI-MS: m/z calculated for C₂₈H₂₈N₂O₆[M+Na]⁺: 511.1912, found 511.2.

2.3.5 Synthesis of 8:

In a 100 mL RB flask, DMF (dry, 5 mL) was taken. Compound **6** (1.02 mmol, 0.5 g) was dissolved in it .The solution was kept stirring for 15 minutes at 0 °C. After that, HOBT(1.02 mmol, 0.13 g) was added and after 5 minutes, EDC.HCl (1.25 mmol, 0.21 g) was added. After that, 1-heptylamine (2.04 mmol, 0.30 mL) was added to the pre cooled reaction mixture. The reaction mixture was left for stirring for 12 hours. Then the solvent was evaporated by using rotary evaporation. The leftover was then dissolved in chloroform. The solution was then washed with 1 N HCl (3×15 mL), Na₂CO₃ (3×15 mL) and brine (3×15 mL). After that, the organic part was dried by using Na₂SO₄ (anhydrous) and chloroform was evaporated by using rotary evaporation. Silica gel column chromatography using chloroform-methanol (19:1) as solvent system was employed to purify the product.

Yield: 38%, 0.3475 g. ¹H NMR (400 MHz, DMSO-*d*6) δ 0.86 (6H, t), 1.21 (20H, m), 2.28, (4H, t), 2.35 (4H, t), 2.74 (2H, m), 2.93 (4H, t), 3.03 (2H, m), 4.54 (2H, t), 7.22 (10H, m), 7.89 (2H, t), 8.31 (2H, t) ppm. ¹³C NMR (100 MHz, DMSO-*d*6) δ 171.52, 170.36, 138.52, 129.76, 128.31, 126.43, 77.73, 66.07, 55.15, 38.55, 33.75, 31.87, 29.74, 28.77, 26.90, 22.58, 15.45,14.28 ppm. ESI-MS:m/z calculated for C₄₂H₅₈N₄O₄[M+Na]⁺: 705.4400, found 705.4150.

2.3.6 Synthesis of 11:

In a RB flask of 100 mL, DMF (3 mL) was taken. Adenine (0.5 g, 3.7 mmol) and activated K_2CO_3 were added to it and the RB was kept for stirring for 30 minutes. After that, propargylbromide (0.88 g, 7.4 mmol) was added drop wise and the reaction mixture was kept for stirring at room temperature for 15 hours. After that, the residual K_2CO_3 was filtered off using suction pump and the organic part was concentrated using rotary evaporation to obtain the crude product. After that Flash column chromatography was employed using methanol-DCM (0.1: 10) solvent system to obtain the final compound. Brownish white powder was obtained.

Yield: 46 %, 0.305 g. ¹H NMR (400 MHz, DMSO *d*6) δ 3.45 (1H, s), 5.01 (2H, s), 7.26 (2H, s), 8.16 (1H, s), 8.18 (1H, s) ppm. ¹³C NMR (100 MHz, DMSO *d*6) δ 32.57, 76.33, 78.59, 119.55, 140.91, 149.74, 153.22, 159.04 ppm. ESI-MS: m/z calculated for C₈H₇N₅[M+H]⁺: 174.0735, found 174.1022.

2.3.7 Synthesis of 12:

In a 100 mL RB flask, acetone (dry, 10 mL) was taken followed by the addition of CuCl (0.11 mmol, 11.44 mg) and TMEDA (0.11 mmol, 0.016 mL). The reaction mixture was kept for stirring for 30 minutes followed by the addition of 9-propargyladenine (0.57 mmol, 0.1 g). After that, the reaction mixture was stirred at open air condition for 24 hours. After that, the remaining solvent was evaporated using rotary evaporation to obtain the crude product. The obtained product was purified by using flash column chromatography using methanol-DCM (0.15: 10) as solvent system to yield the compound. The obtained compound was white powder.

Yield: 38 %, 38.73 mg. 1H NMR (400 MHz, DMSO *d*6) δ 5.02 (2H, s), 7.26 (2H, s), 8.16 (1H, s), 8.18 (1H, s) ppm.

ESI-MS: m/z calculated for $C_{16}H_{12}N_{10}$ [M+H]⁺: 344.1246, found 344.1307.

2.4 Photopolymerization:

The photopolymerization of the F-DA-F and A-DA-A were carried under the UV-Vis light irradiation. In this polymerization, powdered monomers (50mg) were kept on a glass slide and then it the glass slide was placed in a UV chamber for 15 minutes at 25 °C. The chamber was fitted with 6 tubes (12 W each) which provided UV light of wavelength 254 nm. Hence, UV lamp of 96 W was employed to carry out the photopolymerization.

Chapter 3

Result and discussions

The biomolecules functionalized diacetylene based symmetrical monomers F-DA-F (8) and A-DA-A (12) were synthesized and well characterized by ¹H and ¹³C NMR spectroscopy and ESI-MS spectrometry. Further, the self-assembling characteristic of phenylalanine based and adenine based monomers was studied using gelation study using various solvents.

3.1. Gelation study

The phenylalanine based F-DA-F shows highly hydrophobic nature due to presence of alkaline chain present.^[35] The self-assembly properties of F-DA-F was evaluated by gelation study in organic solvents. In 1 mL of organic solvent such as toluene, 20 mmol of the **8** (13.66 mg) was dissolved it in a glass vial.^[25] To completely solubilize the gelator molecules, the mixture was then sonicated for few minutes and then heated at around 105 °C. Then the obtained solution was kept to cool down upto room temperature. The organogel formed was found to be white, self-standing and opaque (Figure 1).



Figure 1.Organogel of F-DA-F monomer in toluene.and dynamic frequency sweep of toluene gel of F-DA-F.

The vial was inverted, and no deformation took place which confirmed that the gelation took place.^[36] The gelation took place by the virtue of self-assembly of F-DA-F which was induced by the factors like hydrogen bonding interactions and π - π staking interactions and hydrophobic interplays of the molecules in F-DA-F.^[37]The process of gelation was tried to perform in various solvents (Table 1). F-DA-Fshows complete soluble nature in the solvents such as acetonitrile, methanol, DMF. However precipitation was observed in hexane, cyclohexane and cycloheptane.

Similarly, the gelation property of adenine functionalized diacetylene monomer A-DA-A was performed in various polar and non-polar solvents. However, gelation of A-DA-A was not observed in various solvents.

Solvent	Observation of 8
	(20 mmol)
Toluene	Gel
Acetonitrile	Precipitate
Cyclohexane	Precipitate
Tetrahydrofuran	Solution
Chloroform	Solution
Dichloromethane	Solution
1,4-dioxane	Solution
Dimethyl formate	Solution
Cycloheptane	Precipitate

Table 1. Gelation study of F-DA-F (8)

3.2 Rheological properties of the gel

Rheology experiment of the organogel was performed to study the firmness of the gel formed.^[38] The stability of the gel is attributed to how intensely the solvent molecules are captured inside the self-assembled 3-D fibrous network of the gel. The more the movement of the solvent molecules is restricted, the stronger the gel is.^[39] Dynamic frequency sweep experiment of the toluene gel of F-DA-F was

done to determine both the storage and loss moduli. G' stands for the storage modulus. It signifies the solid like properties of the gel, which thereby indicates the strength of the gel to prevent its change in shape upon the application of pressure. On the other hand, G" stands for the loss modulus and signifies the liquid like properties of the gel, which denotes the tendency of the gel to flow like a liquid. The required condition for the formation of a strong and stable gel is that the value of G' should remain greater than that of G".^[40] This condition is satisfied in case of organogel of F-DA-F (Figure 1). The frequency sweep data indicates that G' is always higher than G". This shows the viscoelastic nature of organogel of F-DA-F in toluene to form a strong and stable supramolecular gel.

3.3 Polymerization experiments

The self-assembled and orderly arranged diacetylene units undergo topochemical The two photopolymerization. obligatory factors for undergoing photopolymerization are (i) the angle of 45obetween two diyne axes and (ii) the distance between two adjacent divne axes should be 4.9 Å (Figure 2a).^[25]Herein we performed the topochemical photopolymerization of F-DA-F in solid as and gel phase. The peptide functionalized and self-assembled diacetylene monomers underwent photopolymerization through 1,4-addition to form conjugated ene-yne alternated polymer when treated with UV-Vis light. The polydiacetylene based compound F-DA-F formed polydiacetylene covalent organic polymer (PDA-F-COP) in powder as well as gel form.



Figure 2. (a) Schematic mechanism of photopolymerization, (b) solid state photopolymerization of F-DA-F and (c) solid state photopolymerization of A-DA-A.

The color of the monomer F-DA-F changes from white to red (PDA-F-COP) as a result of polymerization (Figure 2b). Similarly, the nucleobase functionalized diacetylene based monomer A-DA-A shows change in color from white to yellow upon treatment with UV rays confirming the formation of adenine functionalized polydiacetylene based covalent organic polymer i.e. PDA-A-COP (Figure 2c). To make sure that the photopolymerization of biomolecule functionalized symmetrical diacetylene based monomers, UV-Vis spectroscopy and Raman spectroscopy analysis were performed.

3.4 UV-Vis spectroscopy analysis

The UV-Vis spectroscopy of F-DA-F was performed by using a Varian Cary100 Bio UV-Visible spectrophotometer. Before recording the spectra, the concentration of all the samples was adjusted to 2 mmol. The absorption spectra was recorded prior to and post UV irradiation of F-DA-F .No peak was observed

in the visible light wavelength region prior to UV irradiation. After UV irradiation, two new peaks were emerged around 528 nm and 490 nm in the visible region indicating the bright red color post polymerization (Figure 3). The new peaks indicated the formation of the COP.



Figure 3.UV-Vis absorbance spectra of F-DA-F and PDA-F-COP.

3.5 Raman spectroscopic Analysis

Raman spectroscopy of F-DA-F was performed by using a Raman spectrometer by JobinYvonHoribaLABRAM-HR. On a glass slide, sample of F-DA-F in powdered form was taken. An excitation wavelength of 537 nm was used to record the by using a He-Ne laser source having an acquisition time of 10 seconds using a 10x objective. A peak at 2263 cm⁻¹was emerged before the UV irradiation of F-DA-F,which indicates the literature value of stretching frequency of 1,3-butadiyne.^[32]The peak at 2263 cm⁻¹ was diminished after UV irradiation and a new peak emerged at 2102 cm⁻¹(Figure 4).^[25] The new peak emerged at 2102 cm⁻¹which indicates the presence of a conjugated C=C bond in the COP. A peak around 1490 cm⁻¹also appeared indicating the presence of C=C bond lying in the ene-yne backbone of COP.



Figure 4.Raman spectrum of F-DA-F and PDA-F-COP.

3.6 Structural analysis

PXRD spectroscopy was carried out using diffractometer by RigakuSmartLabXray having wavelength of 1.54 Å. Powdered samples of F-DA-F before and after polymerization were kept on a glass slide. To study the structural properties, F-DA-F was characterized before after UV irradiation by using this technique.



Figure 5.Wide angle PXRD spectra of the F-DA-F before and after UV light irradiation.

Both of the PXRD spectra show strong diffraction peaks around $2\theta=20^{\circ}$ (Figure 5). There were no major changes in the spectra of F-DA-F before and after the UV-Vis light treatment. This indicates the similarity in the structural orientation of the monomer and the polymer. The diffraction peak observed at $2\theta = 19.6^{\circ}$ (d = 1.12 Å) and at $2\theta = 21.64^{\circ}$ (d = 2.23Å) were the distance between two molecules of F-DA-F. This distance did not alter after polymerization which indicates that interactions like π - π stacking among the aromatic structures and hydrogen bonding which played a crucial role in the self-assembly of F-DA-F, were not affected during the polymerization.^[41]

3.7 Morphological analysis

Morphological studies of F-DA-F before and after UV irradiation were carried out with the help of Scanning Electron Microscopy (SEM) technique.



Figure 6. SEM images of (a) F-DA-F and (b) PDA-F-COP..

SEM images of dried toluene gel of F-DA-F were recorded before and after treatment with UV light. These images showed the fibrous network of F-DA-F with cross-linking prior to and post (Figure 6). After the photopolymerization, the fibrous structure did not show significant change in the morphology.

3.8 Electrochemical properties of PDA-F-COP

The bandgap of PDA-F-COP was estimated with the help of cyclic voltammetry.^[42] The electrochemical measurements were carried out in a single cell with the help of three electrodes. The working electrode was built by drop casting the solutions of F-DA-F and PDA-F-COP (1 mg mL⁻¹ in THF) on glassy carbon (GC) electrode. The counter electrode was made using a Platinum wire. The Ag/AgCl acted as the reference electrode. The working electrode was immersed in the electrochemical cell which contained a solution of 0.1 M tetrabutylammoniumhexafluorophosphate (TBAPF₆) in ACN. The cyclic voltametry (CV) experiments of F-DA-F and PDA-F-COP were performed from -3.0 V to +3.0 V range. From the cyclic voltammogram of PDA-F-COP it was interpreted that the oxidation peak emerged at +1.61 V and the reduction peak emerged at -0.47 V(Figure7). The band gap calculated for PDA-F-COP was 2.08 eV. We have used the following formulae for the estimation of bandgap,^[43]

 $E_{HOMO} = [E_{Ox.(onset)} + 4.8 - E_{ferrocene}] \text{ eV}$ $E_{LUMO} = [E_{Red.(onset)} + 4.8 - E_{ferrocene}] \text{ eV}$

 $E_{\text{band gap}} = [E_{\text{LUMO}} - E_{\text{HOMO}}] \text{ eV}$



Figure 7.Cyclic voltammograms of (a) F-DA-F monomer and (b) PDA-F-COP.

We conclude that there is no reduction or oxidation peak for the cyclic voltammogram of monomer before UV irradiation (Figure 7). The slight downward bump was observed due to the presence of water. Hence, no conjugation was observed here which indicates that the monomer has a large band

gap between HOMO and LUMO which inhibits its usage as a photocatalyst prior to polymerization.

3.9 Photocatalytic performance of PDA-F-COP

The electronic properties of PDA-F-COP were examined by the CV studies. These properties explain the activity of PDA-F-COP as a photocatalyst under UV-Vis light. Through CV experiments, the band gap of PDA-F-COP was calculated to be 2.08 eV. This experimental bandgap data suggests that PDA-F-COP should exhibit Photocatalytic properties under UV-Vis light. It can be concluded that photons possessing energy either equivalent to or having energy greater than that of the band gap of PDA-F-COP (2.08 eV) are capable of producing electrons and holes in the valence band. ^{[44][25]}



Figure 8.Photocatalytic disintegration of Rhodamine B dye in (a) presence of PDA-F-COP and (b) absence of PDA-F-COP under UV-Vis light.

The electrons (e⁻) gets excited from the valence band (VB) and go to the conduction band (CB).On the other hand, the holes (h⁺) generated at the valence band stay there.(Figure 12). Now, these excited e⁻ from the conduction band reacts with O₂ (present in atmosphere or the O₂ dissolved in water) and produces the very reactive superoxide radical (O₂^{-•}) gets. Now, the h⁺ present in the valence band reacts with the H₂O molecule and again generate O₂. The main part in the disintegration of the organic environment pollutant into some simpler and

environment friendly molecules is played by the superoxide radical. The results from the experiment supports that superoxide radical (O_2^{-}) plays a much crucial role in the degradation of organic pollutant dyes.



Figure 9.Schematic diagram of probable mechanism for dye degradation using PDA-F-COP photocatalyst.

It was experimentally proved that the PDA-F-COP which has been synthesized during this project (PDA-F-COP) exhibits activity as a photocatalyst for the disintegration of Rhodamine B dye under UV-Vis light treatment (Figure 8). The percentage disintegration of dye Rhodamine B in the presence of PDA-F-COP as a photocatalyst under UV-Vis light was calculated by using the following equation, where Ai stands for the initial absorbance of the dye and At stands for the absorbance of the dye after time t.

% disintegration = $(A_i - A_i)/A_i$

By using this equation, it was calculated that the photocatalyst PDA-F-COP successfully degraded the dye Rhodamine B upto 87% after 120 minutes of exposure to UV-Vis light. However, no significant disintegration of the dye was observed in the absence of the catalyst under UV light. The PDA-F-COP was found to be quite stable as no noticeable loss of weight was observed for PDA-F-COP after several photocatalytic cycles.

Chapter 4

Conclusion

We have successfully synthesized and fully characterized two polydiacetylene based peptide functionalized ene-yne alternated compounds, Phenylalanine functionalized PDA-F-COP and Adenine functionalized PDA-A-COP. The monomers underwent photopolymerization when irradiated with UV-Vis light and the formation of conjugated polydiacetylene covalent organic polymer took place (PDA-COP). PDA-F-COP exhibited photocatalytic property of degrading pollutant dye Rhodamine B when irradiated with UV-Vis light. Hence the synthesized PDA COPs emerged as tools for the environmental remediation and sustainable development.

APPENDIX-A





Figure 10.¹H NMR (400 MHz, CDCl₃) spectrum of compound 4.



Figure 11.¹³C NMR (100 MHz, CDCl₃) spectrum of compound 4.



Figure 12.¹H NMR (400 MHz, CDCl₃) spectrum of compound 5.



Figure 13.¹³C NMR (100 MHz, CDCl₃) spectrum of compound 5.



Figure 14.¹H NMR (400 MHz, DMSO-*d*6) spectrum of compound 6.



Figure 15.¹³C NMR (100 MHz, DMSO-*d*6) spectrum of compound 6.



Figure 16.¹H NMR (400 MHz, DMSO-*d*6) spectrum of 8.



Figure 17.¹³C NMR (100 MHz, DMSO-*d*6) spectrum of 8.



Figure 18.¹H NMR (400 MHz, DMSO-*d*6) spectrum of compound11.



Figure 19.¹³C NMR (100 MHz, DMSO-*d*6) spectrum of compound 11.



Figure 23.¹H NMR (400 MHz, DMSO-*d*6) spectrum of compound 12.

Mass spectrometry analysis



Figure 21.ESI-MS spectrum of compound 4.



Figure 22.ESI-MS spectrum of compound 5.



Figure 23.ESI-MS spectrum of compound 6.



Figure 24.ESI-MS spectrum of compound 8.



Figure 25.ESI-MS spectrum of compound 11.



Figure 26.ESI-MS spectrum of compound 12.

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