SUSTAINABLE TRANSFORMATION OF PLASTIC ARENES TO FINE CHEMICALS

M.Sc. Thesis

By

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DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE

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Sustainable Transformation of Plastic Arenes to Fine Chemicals

A THESIS

Submitted in partial fulfilment Of the requirements for the award of the degree

Of

Master of Science

by

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DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being reported in this thesis entitled "Sustainable Transformation of Plastic Arenes to Fine Chemicals" in the partial fulfilment of the requirements for the award of the degree of **Master of Science** and submitted in the **Department of Chemistry, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the period from July 2023 to April 2024under the supervision of **Dr. Debayan Sarkar**, Associate Professor, Department of Chemistry, IIT Indore.



Nabanita Dey

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

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M.Sc. 4th Semester

Department of Chemistry

DEDICATION

I dedicate this thesis to my beloved parents who have been the constant source of my motivation, guidance, strength, who have always believed in me even when I thought of giving up, who continually provide me with their emotional, spiritual and financial support.

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ABSTRACT

Plastics, synthetic or semisynthetic polymers are considered to have wide range of applications owing to their great adaptability, flexibility, long-durability, light-weight, low-cost, corrosion resistance and moisture resistance properties. Due to numerous commercial applications, the plastic production has been significantly increasing worldwide with each passing day creating a pervasive and nearunmanageable threat called 'Plastic Pollution' as most of the plastics ever made is no longer in use, instead get stagnant in landfill or get released into the environment. This plastic pollution has detrimental impacts in all three systems e.g., terrestrial, marine and atmosphere and it's adversely effecting both Flora and Fauna of this world. Therefore, the main idea of our work is to convert the commercial plastic wastes into fine chemicals approaching through a sustainable pathway. We are mainly focusing on the plastics having an aromatic core and trying to regenerate the raw materials and some value-added products without involving any purification or separation in between rather making the whole conversion one-pot. Hopefully, our strategy of chemical recycling of plastics without using any toxic reagent or extreme harsh condition will lead us to synthesize some desirable new products and will make some contribution in saving the landfill space and preventing pollution.

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LIST OF ACRONYMS

Abbreviation/Symbol

Meaning

1. SPI	Society of Plastic Industry
2. THF	Tetrahydrofuran
3. HMPA	Hexamethylphosphoramide
4. GSW	Galvanised steel wire
5. LiBr	Lithium bromide
6. Cs_2CO_3	Cesium Carbonate
7. DCM	Dichloromethane
8. CH ₃ CN	Acetonitrile
9. W	Watt
10. p-TsOH.H ₂ O	Paratoluenesulfonic acid monohydrate
11. nm	Nanometre
12. C_3N_4	Carbon nitride
13. NaOH	Sodium hydroxide
14. KOH	Potassium hydroxide
15. AgNTf ₂	Silver triflimide
16. MeOH	Methanol
17. TBD	1,5,7-triazobicyclo[4,4,0]dec-5-ene
18. ppm	parts per million
19. 2-Me-THF	2-methyl tetrahydrofuran
20. Na ₂ CO ₃	Sodium Carbonate
21. TBAB	Tetrabutyl ammonium bromide
22. DEAD	Diethyl azodicarboxylate
23. CF ₃ SO ₃ H	Trifluoromethane sulfonic acid
24. $K_2S_2O_8$	Potassium peroxodisulfate
25. DIAD	Diisopropyl azodicarboxylate
26. RFTA	Riboflavin tetraacetate
27. CD	Compact Disc
28. TLC	Thin Layer Chromatography
29. BPA	Bisphenol A
30. TEMPO	2,2,6,6- tetramethyl-1-piperidinyloxy
31. EPS	Expanded Polystyrene
32. DTBAD	Ditert-butyl azodicarboxylate
33. DBAD	Dibenzyl azodicarboxylate
34. NMR	Nuclear Magnetic Resonance
35. FT-IR	Fourier Transform Infrared Radiation
36. LC-MS	Liquid chromatography-mass spectrometry
37. EtOAc	Ethyl acetate
38. GC-MS	Gas Chromatography- mass spectrometry
39. R.B.	Round Bottom
40. K ₂ CO ₃	Potassium Carbonate

NOMENCLATURE

equivalent
millimole
milligram
hour
minutes
room temperature
degree Celsius
millilitre
chemical shift

A. INTRODUCTION:

The word Plastic originally came from "pliable" which means "easily shaped". Basically, Plastics are known as polymers or a "long chains of <u>monomers</u>", which are attached to other resembling subunits to form a polymer which are mixed with some potentially toxic additives to make those lightweight, strong, durable, corrosion-resistant materials ^[1]. These advantageous properties of plastic have led us to consider it to be a 'material of 1000 uses', starting from packaging, clothing, automobile sector to the manufacturing industry of medical equipment.

Plastics are classified mainly into two categories depending on their chemical structure and temperature resistance e.g., Thermoplastics and Thermosetting plastics. Thermoplastics have weak intermolecular forces between the polymeric chains present in it and this type of plastics melt or soften on heating and harden after cooling. There are many thermoplastics available in our day-to-day life like Polystyrene (PS), Polycarbonate (PC), Polyurethane (PU), Polyethylene terephthalate (PET), Acrylonitrile butadiene styrene (ABS) etc.

Thermosetting plastics have strong covalent bond or cross-linking between the existent polymeric chains and this type of plastics remains hard even after heating. Thermosetting plastics are very widely used in industrial fields and the most common examples of thermosetting plastics are Bakelite, Melamine-resin, Urea-formaldehyde resin etc.^[2-3]

TABLE 1: The example of some of the real-life commodities made of different plastics along with the Society of the Plastic Industry (SPI) Codes for that particular plastic.

SPI Code	Plastic	Real life uses			
1	PET	Water bottles.	soft drink		
		bottles,	video-tapes,		
		microwave containers etc.			

6	Polystyrene	Disposable cutlery sets, packaging of goods, Styrofoam, egg cartons, CD cases
7	Polycarbonate	Compact discs, plastic lenses, helmets, safety glasses, suitcases, canes of soft drinks etc.
7	ABS	Plastic toys, printers, vacuum cleaner etc.
7	Polyurethane	Daily use kitchen sponge, sleeping mattresses, carpets, flexible couches etc.
7	Bakelite	Plastic jewellery, electrical sockets, switches, handle of pressure cooker, telephones etc.

Structures of some Aromatic Plastics which we are mainly focusing on for our work is shown below.^[3]



Figure 1: Chemical Structures of some Aromatic Plastics



Polycarbonate





Polystyrene





Polyethylene terephthalate



ABS

Polyurethane Bakelite Figure 2: Real life Plastic commodities

Instead of various applications in modern human civilization, plastics are found to be persistent polluters disrupting the delicate balance of ecosystems and adversely effecting human health as more than 50% of the plastics ever made are never reused or recycled rather illegally dumped or disposed to the landfills or released into the environment by burning.

Needless to say, this global plastic pollution is causing an alarming threat to all the environmental niches starting from mountain to ocean and consequently, severely undermining the wildlife, aquatic lives and our social-well-being with its detrimental impacts.^[2] It is reported that more than 12 million metric ton plastics enter into the environment every year and the scenario is getting worsened each day due to the non-biodegradability of these single-use plastics. Therefore, this is the high time for us to boost the recycling rates of the waste plastic wastes to save our mother nature.

B. OBJECTIVE:

Undoubtedly, the wonder product, plastic has become ubiquitous in our everyday life due its unique and beneficial properties discussed earlier. But unfortunately,50% of all the plastics produced, are single use items.^[1] Consequently, production of plastics is increasing exponentially and more than 300 million tons of plastic wastes are getting into the environment every year in many ways. The landfills never destroy the waste plastics rather conserves the poison for year and over the years, these plastics only degrade into microplastics introducing a new pollutant for the world.^[3]

So far, there are very few works reported on Chemical recycling and upcycling of real-life plastic wastes. For our project, we are mainly targeting the waste plastics having an aromatic core and we are trying to transform the waste plastic to some value-added new products with some desirable properties. Our main goal is to do the transformation without using any toxic, expensive metal catalyst or any harmful reagent rather we are focusing on doing the conversion keeping the reaction conditions mild and keeping the whole process 'one-pot' to reduce the chemical waste, to save time and to simplify the process keeping the practical aspects in mind.

We are hopeful that if our strategy chemical recycling or upcycling of commercial plastic waste successfully works, it will definitely have a contribution in making the future better by saving landfill space, producing desirable raw materials, reducing energy consumption, tackling climate change by reducing greenhouse gas emission and last but not the least by promoting sustainability. ^[7-8]



Scheme 1: General objective of our work.

C. MOTIVATION:

The biggest motivation behind this work is the lack of 'end-of-life' data of the most versatile and over-used material called plastic.

Using the traditional mechanical recycling process, we are only able to grind the plastics into some microplastics (which also act as poison for atmosphere) consuming a huge amount of energy. ^[3] Mechanical recycling of waste plastic often leads us to obtain poor quality end-products which is the major drawback of traditional recycling of plastics. Whereas the chemical recycling can be a better solution to this prevalent challenge of plastic pollution as it has the potential to transform the waste into some fine chemicals with desirable properties which can be used as raw materials for various required applications by completely disrupting the chemical structure of the polymers.^[5] Moreover, mechanical recycling is not suitable for the heavy weight plastics, whereas Chemical recycling technologies can expand the types of plastics that can be recycled. We believe this will result in a paradigm shift from a 'waste-orientated' to a 'resourceorientated' economy helping to maintain a circular economy for the real- life plastic wastes.^[6]

Though a completely 'Plastic-free Earth' might be an unrealistic solution to this persistent problem considering the benefits and utility of the plastic products, it's possible for us to embark on a journey of plastic recycling proceeding through a sustainable pathway to keep them in cycle reducing the waste of natural resources, preventing the carbon emission and replacing incineration.

D. LITERATURE SURVEY:

From the literature survey, we have found the following previously reported works on chemical recycling, upcycling and depolymerization of different plastics.



Scheme 2: Electrochemical dearomatisation of Polystyrene

In 2021 Sarlah et al. reported the electrochemical dearomatisation of polystyrene plastic using dimethylurea, HMPA and lithium bromide and for the reaction DC power was used. ^[8]



Scheme 3: Catalytic oxidation of Polystyrene

In 2022 Zhang et al. developed a new method for catalytic oxidation of polystyrene using acetonitrile as solvent and obtained oxidized useful products out of waste polystyrene plastic.^[9]



Scheme 4: Photochemical oxidation of Polystyrene

In 2022 Stache and group gave a new direction in chemical upcycling of plastic by developing a new strategy of photochemical oxidation of polystyrene plastic using ferric chloride.^[10]



Scheme 5: Chemical upcycling of Polycarbonate plastic

In 2023, Onida et al. converted polycarbonate to vinylene carbonates through organocatalysis using an organic base and benzoin.^[11]



Scheme 6: Chemical upcycling of Polycarbonate plastic through amidation

In 2021, Kim and group synthesized a value-added new molecule starting from waste polycarbonate plastic through one-pot C-H amidation.^[12]



Scheme 7: Chemical deconstruction of Polyurethane foam

In 2022, Skrydstrup et al. reported tert-amyl alcohol mediated deconstruction of polyurethane foam to its monomeric unit performing the reaction inert condition.^[13]



Scheme 8: Chemical recycling of PET plastic

In 1997, Chemical recycling of waste plastic water bottles to its monomeric units was reported by Daniel and co-workers.^[14]

E. SCOPE OF WORK:

It is very evident that Plastic pollution has become a global challenge and it is a great menace to our planet and all its inhabitants. So, to have a safer, cleaner and sustainable world chemical recycling and upcycling of plastic wastes will be the best possible solution in every aspect.^[1] Even if the plastic production is banned today, there's still an urgent need to recycle the plastic wastes already present in our environment.^[3]

Though, there are many conventional recycling processes of waste plastics known, we have to find some less hazardous, cost-effective and high performing method to combat with this prevailing plastic pollution. Under this context, we anticipate a sustainable approach towards plastic recycling either via dearomatisation, post functionalization or any other environment-friendly chemical pathway will find broader use in plastic diversification and in getting back the chemical feedstock. ^[7-8] In future, the obtained chemicals or the transformed molecules with comparatively less complex structure can be utilized in a diverse range of industrial applications or sometimes can be further used for plastic production^[4] Hence, if the incinerated and landfilled waste can be moved to disposal following a sustainable chemical recycling or upcycling strategy, we will definitely be able to create a better world to live in lowering the carbon footprint of products and by enabling the production of high- quality end products. Along with offering ample number of environmental benefits, this recycling technique can also improve the global economy by reducing energy and raw materials consumption, saving the marine environment from severe threat of plastic pollution and creating new job opportunities.

A. OPTIMIZATION OF REACTION CONDITION:



• **TABLE 2:** Detailed optimisation table for chemical recycling of waste polycarbonate plastic to its monomeric unit.^a

Entry	Solvent [15 ml]	Base Catalyst [equiv.]	Reaction Time	Reaction Temperature	Yield of BPA ^b
1.	THF	CS_2CO_3	4h	65 °C	61%
2.°	THF/CH ₃ CN [2:1]	CS ₂ CO ₃	4h	65 °C	78%
3.	DCM	CS_2CO_3	4h	65 °C	49%
4.	DCM/CH ₃ CN [2:1]	CS_2CO_3	4h	65 °C	59%
5.	THF/H ₂ O [2:1]	CS_2CO_3	4h	65 °C	33%
б.	CH ₃ CN	CS_2CO_3	4h	65 °C	0%
7.	THF/CH ₃ CN [2:1]	CS ₂ CO ₃	8h	r.t.	Trace
8.	THF/CH ₃ CN [2:1]	K ₂ CO ₃	4h	65 °C	57%
9. ^d	THF/CH ₃ CN [2:1]	CS ₂ CO ₃	4h	65 °C	75%
10.	THF/CH ₃ CN [2:1]	Na ₂ CO ₃	4h	65 °C	51%
11. ^e	THF/CH ₃ CN [2:1]	CS ₂ CO ₃	4h	65 °C	73%
12.	H ₂ O	CS ₂ CO ₃	4h	65 °C	0%

^areaction conditions: 500 mg of waste plastic, base catalyst (0.3 equiv.), solvent (15 ml); ^bIsolated yields; ^cstarting material waste CD fragments, ^dstarting material waste safety glass, ^estarting material waste bottle cap; Equivalence was calculated based on the molar mass of one monomeric unit [254.29 g/mol] present in the plastic.



TABLE 3: Detailed optimisation table for chemical upcycling of waste polycarbonate plastic through photocatalytic amination.^a

Entry	Solvent [4 ml]	Photocatal yst [mol%]	Light wavelength	Additive [mmol]	Reaction time	Yield ^b
1. ^c	THF/CH ₃ CN (1:1)	RFTA	455 nm	TBAB	3h	50%
2.	DCM/CH ₃ CN (1:1)	RFTA	455 nm	TBAB	3h	36%
3.	CH ₃ CN	RFTA	455 nm	TBAB	3h	0%
4.	THF/CH ₃ CN (1:1)	None	455 nm	TBAB	3h	Trace
5.	THF/CH ₃ CN (1:1)	Rose bengal	455 nm	TBAB	3h	33%
6.	THF/CH ₃ CN (1:1)	RFTA	527 nm	TBAB	3h	0%
8.	THF/CH ₃ CN (1:1)	Eosin blue	455 nm	TBAB	3h	Trace
9.	THF/CH ₃ CN (1:1)	RFTA	455 nm	None	3h	29%
10.	THF/CH ₃ CN (1:1)	Eosin Y	455 nm	TBAB	3h	23%
11.	THF/CH ₃ CN (1:1)	Methylene blue	455 nm	TBAB	3h	19%
12.	THF/CH ₃ CN (1:1)	RFTA	No light	TBAB	3h	NR
13.	THF/CH ₃ CN (1:1)	RFTA	455 nm	TBAB	3h	NR
14. ^d	THF/CH ₃ CN (1:1)	RFTA	455 nm	TBAB	3h	21%
15.	THF/CH ₃ CN (1:1)	None	455 nm	None	3h	Trace

Entry	Solvent [4 ml]	Photocatal yst [mol%]	Light wavelength	Additive [mmol]	Reaction time	Yield
16.	THF/CH ₃ CN (1:1)	RFTA	455 nm	TBAI	3h	38%
17.	DCM/CH ₃ CN (1:1)	RFTA	455 nm	KBr	3h	16%
18.	H ₂ O	RFTA	455 nm	TBAB	3h	0%
19.	H ₂ O/CH ₃ CN (1:1)	None	455 nm	TBAB	3h	0%
20.	THF/CH ₃ CN (1:1)	Rose bengal	455 nm	TBAB	3h	33%
22. ^e	THF/CH ₃ CN (1:1)	RFTA	455 nm	TBAB	3h	48%
23. ^f	THF/CH ₃ CN (1:1)	RFTA	455 nm	TBAB	3h	48%
24. ^g	THF/CH ₃ CN (1:1)	RFTA	455 nm	TBAB	3h	44%

^areaction conditions: 200 mg of waste plastic, base catalyst (0.3 equiv.), solvent (4 ml), photocatalyst (1 mol%), additive (0.1 mmol), azodicarboxylate [2 eq.]; ^bIsolated yields; ^cstarting material waste safety glass, ^estarting material waste CD fragments, ^fstarting material waste bottle cap; ^ereaction performed in nitrogen atmosphere; ^greaction in presence of oxygen balloon ; Equivalence was calculated based on the molar mass of one monomeric unit [254.29 g/mol] present in the plastic.

TABLE 4: Detailed optimisation table for chemical upcycling of waste

 polycarbonate plastic through photocatalysis.^a



Entry	Solvent [4 ml]	Aminating Agent [equiv.]	Oxidant [equiv.]	Wavelength of light	Photocatalyst [mol%]	Reaction time	Yield ^b
1.	THF/CH ₃ CN (1:1)	PTZ	$K_2S_2O_8$	455 nm	Fluorescein	6h	51%
2.°	DCM/CH ₃ CN (1:1)	PTZ	$K_2S_2O_8$	455 nm	Fluorescein	6h	63%
3.	DCM/CH ₃ CN (1:1)	PTZ	None	455 nm	Fluorescein	6h	Trace
4.	DCM/CH ₃ CN (1:1)	PTZ	$K_2S_2O_8$	No light	Fluorescein	бh	0%
5.	CH ₃ CN	PTZ	$K_2S_2O_8$	455 nm	Fluorescein	6h	0%
6.	DCM/CH ₃ CN (1:1)	PXZ	$K_2S_2O_8$	455 nm	None	6h	32%
7.	THF/CH ₃ CN (1:1)	PXZ	$K_2S_2O_8$	455 nm	None	бh	28%
8.	DCM/CH ₃ CN (1:1)	PTZ	$Na_2S_2O_8$	455 nm	Fluorescein	6h	46%
9.	DCM/CH ₃ CN (1:1)	PXZ	$K_2S_2O_8$	455 nm	Fluorescein	6h	51%
10.	DCM/CH ₃ CN (1:1)	PTZ	$K_2S_2O_8$	455 nm	Eosin blue	бh	41%
11.	DCM/CH ₃ CN (1:1)	PTZ	$K_2S_2O_8$	455 nm	None	бh	43%
12.	DCM/CH ₃ CN (1:1)	PTZ	$K_2S_2O_8$	455 nm	Eosin Y	бh	49%
13. ^d	DCM/CH ₃ CN (1:1)	PTZ	$K_2S_2O_8$	455 nm	Fluorescein	6h	34%
14.	DCM/CH ₃ CN (1:1)	PTZ	$K_2S_2O_8$	527nm	Fluorescein	6h	Trace
15.	DCM	PTZ	$K_2S_2O_8$	455 nm	Fluorescein	6h	51%
16. ^e	DCM/CH ₃ CN (1:1)	PTZ	$K_2S_2O_8$	455 nm	Methylene blue	6h	53%

PTZ: Phenothiazine, PXZ: Phenoxazine.

^areaction conditions: 200 mg of waste plastic, oxidant (2 equiv.), solvent (4 ml), photocatalyst (1 mol%), aminating agent (2 equivalent); ^bIsolated yields; ^cstarting material waste bottle cap, ^estarting material waste safety glass; ^dreaction performed in argon atmosphere; ^greaction in presence of oxygen balloon; Equivalence was calculated based on the molar mass of one monomeric unit [254.29 g/mol] present in the plastic.
B. EXPERIMENTAL DETAILS:

- Material and instrumentation: All the required chemicals were brought from Sigma Aldrich, TCI, Spectrochem and Avra. The mass spectrometry [ESI-MS] was performed using Bruker MicrOTOF-Q II that uses positive- mode electron spray ionization. ¹H NMR [500 MHz] and and ¹³C NMR (125 MHz) were recorded in deuterated solvent (D₂O) using Bruker Advance 500.
- General Procedure for the reactions:

• General Experimental Procedure A:

500 mg (1.96 mmol) of waste Polycarbonate plastic taken in a ovendried R.B were dissolved in 10 ml THF and then 192.19 mg (0.59 mmol) of Cs₂CO₃ was added to that solution as a base catalyst and then 5ml of acetonitrile was added to the same solution. After addition of all the reactants the reaction mixture was refluxed for 4 hours at 65 °C. The reaction was monitored by TLC checking and after the completion of the reaction, the reaction was quenched adding 1 ml of distilled water. Then the organic layer was separated using ethyl acetate and water and after that organic part was dried over anhydrous Na₂SO₄. Next, the solvent was concentrated under reduced pressure and the pure product was isolated by performing silica gel column chromatography using Ethyl acetate and Hexane in a ratio of 1:9.

After isolation, the product was kept undisturbed for 3 days in a mixture of 2 ml DCM and 2 ml hexane for recrystallization and after 3 days the obtained needle-like white crystals were dried in oven for 2 hours and then it was weighed.



Scheme 9: Chemical recycling of different type of polycarbonate 13



Figure 3: Conversion of waste polycarbonate bottle cap, waste CD fragments and waste safety glass to bisphenol A.

• General Experimental Procedure B:

An oven dried sample vial with stir bar was charged with 200 mg (0.78 mmol) of waste polycarbonate plastic dissolved in a 4 ml solvent mixture and then 76.82 mg (0.235 mmol) of Cs₂CO₃ and other additive TBAB [35 mg, 0.108 mmol] were added to that solution and the reaction mixture was stirred for 2 hours at room temperature under the illumination of a blue LED light [455 nm] of power 0.9W. The vial was sealed with a cap equipped with Teflon septum. After 2 hours, a photocatalyst RFTA in catalytic amount [5 mg, 0.009 mmol] and 2 equivalent of an azodicarboxylate were added to the same sample vial as an aminating agent and then the reaction mixture was stirred for another 1-1.5 hours at room temperature in the same photoreactor connected with water circulation. By checking TLC the reaction was monitored and once the TLC indicated the total consumption of the aminating agent the reaction was quenched by removing the reaction mixture from the photoreactor and by adding 1ml distilled water to the solution. Then the organic layer was separated using ethyl acetate and water and then the organic part was dried over anhydrous Na₂SO₄. Next, the solvent was concentrated under reduced pressure and the pure product was isolated by performing silica gel column chromatography using the mixture of Ethyl acetate and Hexane as the mobile phase and the isolated yield of the obtained product was checked.



Scheme 10: Chemical upcycling of different type of polycarbonate plastic through Photocatalytic amination.

General Experimental Procedure C:

An oven dried sample vial with stir bar was charged with 200 mg (0.78 mmol) of waste polycarbonate plastic dissolved in a 4 ml solvent mixture. To the mixture 2 equiv. of K₂S₂O₈ (425mg, 1.57 mmol) and 2 equivalent of Diarylamine were added and then the reaction mixture was stirred for 6 hours at room temperature under the illumination of a blue LED light [455 nm] of power 0.9W in presence of catalytic amount of methylene blue (5mg, 0.015 mmol) The vial was sealed with a cap equipped with Teflon septum. By checking TLC the reaction was monitored and once the TLC indicated the total consumption of the aminating agent the reaction was quenched by removing the reaction mixture from the photoreactor and by adding 1ml distilled water to the solution. Then the organic layer was separated using ethyl acetate and water and then the organic part was dried over anhydrous Na₂SO₄. Next, the solvent was concentrated under reduced pressure and the pure product was isolated by performing silica gel column chromatography using the mixture of Ethyl acetate and Hexane as the mobile phase and the isolated yield of the obtained product was checked.



Scheme 11: Chemical upcycling of different type of polycarbonate plastic

through Photocatalysis



Figure 4: Photoreaction Set up



Figure 5: Different reaction mixture after completion of reaction where starting material was waste polycarbonate plastic.

• SUBSTRATE SCOPE:



C. CONTROL EXPERIMENT:

1. Radical trapping experiment for Chemical upcycling of waste polycarbonate plastic through photocatalytic amination [with TEMPO]:

An oven dried sample vial with stir bar was charged with 200 mg (0.78 mmol) of waste polycarbonate plastic dissolved in a 4 ml solvent mixture and then 76.82 mg (0.235 mmol) of Cs₂CO₃ and other additive TBAB [35 mg, 0.108 mmol] were added to that solution and the reaction mixture was stirred for 2 hours at room temperature under the illumination of a blue LED light [455 nm] of power 0.9W. The vial was sealed with a cap equipped with Teflon septum. After 2 hours, a photocatalyst RFTA in catalytic amount [5 mg, 0.009 mmol], 0.6 equivalent diisopropyl azodicarboxylate [330 microlitre] and 3 of equivalent [365.62 mg, 2.33 mmol] of radical quencher TEMPO were added to the same sample vial as an aminating agent and then the reaction mixture was stirred for another 1-1.5 hours at room temperature in the same photoreactor connected with water circulation. Reaction mixture was analysed by mass spectrometry for any possible radical trapped adduct.



Radical trapped adduct: **LCMS** (ESI,m/z): Calculated for [C₂₆H₅₀N₄O₆+Cl]⁺:549.3412; found: 549.3582



Figure 6: The LC-MS analysis of the reaction mixture of radical trapping experiment with TEMPO.

2. Radical trapping experiment for Chemical upcycling of waste polycarbonate plastic through photocatalytic amination [with BHT]:

An oven dried sample vial with stir bar was charged with 200 mg (0.78 mmol) of waste polycarbonate plastic dissolved in a 4 ml solvent mixture and then 76.82 mg (0.235 mmol) of Cs₂CO₃ and other additive TBAB [35 mg, 0.108 mmol] were added to that solution and the reaction mixture was stirred for 2 hours at room temperature under the illumination of a blue LED light [455 nm] of power 0.9W. The vial was sealed with a cap equipped with Teflon septum. After 2 hours, a photocatalyst RFTA in catalytic amount [5 mg, 0.009 mmol], 2 equivalent of diisopropyl azodicarboxylate and 3 equivalent [515.16 mg, 0.78 mmol] of radical quencher BHT were added to the same sample vial as an aminating agent and then the reaction mixture was stirred for another 1-1.5 hours at room temperature in the same photoreactor connected with water circulation. Reaction mixture was analysed by mass spectrometry for any possible radical trapped adduct.



Radical trapped adduct: LCMS (ESI,m/z): Calculated for [C₃₈H₆₀N₂O₆+Na]⁺:663.1932; found: 663.1668.



Figure 7: The LC-MS analysis of the reaction mixture for radical trapping experiment with BHT.

3. Radical trapping experiment for Chemical upcycling of waste polycarbonate plastic through photocatalytic amination [with BHT]:



An oven dried sample vial with stir bar was charged with 200 mg (0.78 mmol) of waste polycarbonate plastic dissolved in a 4 ml solvent mixture. To the mixture 2 equiv. of $K_2S_2O_8$ (425mg, 1.57 mmol), 2 equivalent of Phenothiazine (310.86 mg,1.56 mmol) and 3 equivalence of BHT [515.16 mg, 2.33mmol] were added and then the reaction mixture was stirred for 6 hours at room temperature under the illumination of a blue LED light [455 nm] of power 0.9W in presence

of catalytic amount of methylene blue (5mg, 0.015 mmol) The vial was sealed with a cap equipped with Teflon septum. Reaction mixture was analysed by mass spectrometry for any possible radical trapped adduct.

Yield of compound [3g] was 0%.

Radical trapped adduct [P]: LCMS (ESI,m/z): Calculated for [C₁₇H₃₁NSO-H]⁺:416.3124; found: 416.6461.



Figure 8: The LC-MS analysis of the reaction mixture for radical trapping experiment with BHT.

Radical trapped adduct [Q]: LCMS (ESI,m/z): Calculated for [C43H56O4+H]⁺:637.5230; found: 637.5650.



Figure 9: The LC-MS analysis of the reaction mixture for radical trapping experiment with BHT.

• Light and Dark Experiments:

For reaction scheme 10: An oven dried sample vial with stir bar was charged with 200 mg (0.78 mmol) of waste polycarbonate plastic dissolved in a 4 ml solvent mixture and then 76.82 mg (0.235 mmol) of Cs_2CO_3 and other additive TBAB [35 mg, 0.108 mmol] were added to that solution and the reaction mixture was stirred for 2 hours at room temperature under the illumination of a blue LED light [455 nm] of power 0.9W. The vial was sealed with a cap equipped with Teflon septum. After 2 hours, a photocatalyst RFTA in catalytic amount [5 mg,

0.009 mmol], 0.6 equivalent of diisopropyl azodicarboxylate [100 microlitre] The reaction mixture was irradiated with blue LED light (458nm), which was switched between light and dark every 0.5 hour. The reaction aliquot was taken out after every interval of 0.5 hour, quenched with water, and the organic part was dissolved in ethyl acetate, and the NMR analysis was performed. NMR yields were determined using mesitylene as an internal standard.

Time [min]	Light Source	Yield
30	On	12%
60	Off	13%
90	On	26%
120	Off	28%
150	On	37%
180	Off	38%



Figure 10: Light-dark experiment plot.

D. Scale up Reaction for Chemical Upcycling of Waste Polycarbonate with Azodicarboxylates:



An oven dried sample vial with stir bar was charged with 700 mg (2.75 mmol) of waste polycarbonate plastic dissolved in a 4 ml solvent mixture and then 268.80 mg (0.824 mmol) of Cs₂CO₃ and other additive TBAB [120 mg, 0.372 mmol] were added to that solution and the reaction mixture was stirred for 2 hours at room temperature under the illumination of a blue LED light [455 nm] of power 0.9W. The vial was sealed with a cap equipped with Teflon septum. After 2 hours, a photocatalyst RFTA in catalytic amount [10 mg, 0.018 mmol] and 2 equivalent of diisopropyl azodicarboxylate [1.15 ml] were added to the same sample vial as an aminating agent and then the reaction mixture was stirred for another 1.5 hours at room temperature in the same photoreactor connected with water circulation. By checking TLC the reaction was monitored and once the TLC indicated the total consumption of the aminating agent the reaction was quenched by removing the reaction mixture from the photoreactor and by adding 1ml distilled water to the solution. Then the organic layer was separated using ethyl acetate and water and then the organic part was dried over anhydrous Na₂SO₄. Next, the solvent was concentrated under reduced pressure and the pure product was isolated by performing silica gel column chromatography using the mixture of Ethyl acetate and Hexane as the mobile phase and the isolated yield of the obtained product was checked.

E. UV-VISIBLE EXPERIMENT:

UV-VIS spectra of starting polycarbonate material [0.025 mM], cesium carbonate [0.025 mM], Tetrabutylammonium bromide [0.025 mM] in mixture of THF and acetonitrile [1:1] were recorded.

UV-VIS spectra of mixtures of polycarbonate plastic and cesium carbonate [0.025 mM PC+ 0.025 mM Cs₂CO₃], mixture of polycarbonate plastic and TBAB [0.025 mM PC+ 0.025 mM TBAB] and a mixture of waste polycarbonate, cesium carbonate and TBAB [0.025 mM PC + 0.025 mM PC + 0.025 mM TBAB] were recorded in mixture of THF and acetonitrile [1:1].

The plastic shows absorbance at deep UV region, cesium carbonate shows maximum absorbance at 237nm and TBAB shows maximum absorbance at 232 nm. The mixture of cesium carbonate, plastic and TBAB shows maximum absorbance at 443 nm.



Figure 11: UV- VIS absorption spectra of different substances

• Absorption Spectra of Compound [3g] and [3h]:

The UV absorption spectra were recorded for 0.025 mM solution of both the compound [3g] and [3h] in acetonitrile. Along with the compounds the absorption spectra for 0.025 mM Phenothiazine and 0.025mM of Phenoxazine were also recorded in acetonitrile solvent as one of the main reagents in synthesizing compound [3h] and [3g] respectively.

Phenoxazine shows maximum absorbance at 347 nm while compound [3g] shows maximum absorbance at 445 and 356 nm.

Phenothiazine shows maximum absorbance at 271 nm while compound [3h] shows maximum absorbance at 512 nm.



Figure 12: UV-VIS absorption spectra of compound [3g] and Phenoxazine



Figure 13: UV-VIS absorption spectra of compound [3h] and Phenothiazine

F.FLUORESCENCE QUENCHING EXPERIMENTS:

All the sample solutions were prepared freshly before performing the experiments.

Fluorescence quenching of 1. for one-pot amination polycarbonate with azodicarboxylates: Initially, 1µM solution of RFTA was prepared in Acetonitrile. 100 µL of this stock solution was taken in a quartz cuvette and diluted with acetonitrile up to a volume of 2.0 mL. To this 0.05µM solution of RFTA, 0.1 Μ solution of polycarbonate plastic/Di-tert butyl azodicarboxyalte/ TBAB were added successively and change in the emission intensity was observed. In all cases, the solutions were excited at a wavelength of 445 nm and the fluorescence emission data was collected at a wavelength of 520 nm. Corresponding Stern-Volmer graphs were constructed in every case to identify the quencher species.

Fluorescence emission spectra of RFTA with the varying concentration of Polycarbonate plastic:



Fluorescence emission spectra of RFTA with the varying concentration of Di-tert butyl azodicarboxylate:



Fluorescence emission spectra of RFTA with the varying concentration of TBAB:



Fluorescence emission spectra of RFTA with the varying concentration of Bisphenol A:



STERN-VOLMER PLOT:



2.Fluorescence quenching for one-pot amination of polycarbonate with Phenothiazine:

Initially, 2μ M solution of Fluorescein was prepared in Acetonitrile. 100 μ L of this stock solution was taken in a quartz cuvette and diluted with acetonitrile up to a volume of 2.0 mL. To this 1 μ M solution of Fluorescein, 0.1 M solution of polycarbonate plastic/Phenothiazine/K₂S₂O₈ were added successively and change in the emission intensity was observed. In all cases, the solutions were excited at a wavelength of 460 nm and the fluorescence emission data was collected at a wavelength of 531 nm. Corresponding Stern-Volmer graphs were constructed in every case to identify the quencher species. Fluorescence emission spectra of Fluorescein with the varying concentration of Polycarbonate plastic:



Fluorescence emission spectra of Fluorescein with the varying concentration of K₂S₂O₈:



Fluorescence emission spectra of Fluorescein with the varying concentration of Phenothiazine:



• STERN-VOLMER PLOT:



A. RESULT AND DISCUSSION:

Characterization data of compound 1p, 3a-3i:



4,4'-(propane-2,2-diyl) diphenol[1p]: The titled compound was synthesized following general procedure A in 78% yield [350.09 mg] as white needle-like crystals; eluted in 10% ethyl acetate and hexane (v:v) in silica gel column chromatography; ¹H NMR (500 MHz, CDCl₃): δ 7.02 (d, *J* = 8.9 Hz, 4H), 6.65 (d, *J* = 8.7 Hz, 4H), 4.57 (s, 2H), 1.55(s, 6H), ¹³C NMR (126 MHz, CDCl₃): δ 153.2, 143.3, 127.9, 114.7, 41.7, 31.0, 137.9, **IR frequency:** 3300-3400 cm⁻¹[O-H stretching],3028 cm⁻¹ [aromatic C-H stretching],1358-1506 cm⁻¹ [C-H bending], 1100-1400 cm⁻¹ [C-O stretching]; **LCMS** (ESI, *m/z*): Calculated for C₁₅H₁₆O₂ [M]: 228.2901, found- 228.1100.



Diethyl 1-(2-hydroxy-5-(2-(4-hydroxyphenyl) propan-2-yl) phenyl) hydrazine-1,2-dicarboxylate [3a]: The titled compound was prepared following the general procedure B in 50% yield [156.85 mg] as a pale yellowish oil; eluted in 12% ethyl acetate and hexane (v:v) in silica gel column chromatography; ¹H NMR (500 MHz, CDCl₃): δ 7.22(d, *J* = 8.4 Hz, 1H), 7.17-7.13 (m, 3H), 7.08 (d, *J* = 9.2 Hz, 1H), 6.74 (d, *J*=8.7 Hz, 2H), 6.38 (s, 1H), 6.00 (s, 1H), 5.14 (s, 1H), 4.38-4.29 (m, 2H), 4.26-4.19 (m, 2H), 1.62 (s, 6H), 1.35-1.27 (m, 6H); ¹³C NMR (126 MHz, CDCl₃): δ 157.1, 155.4, 153.9, 152.3, 152.0, 148.5, 141.8, 128.0, 127.8, 120.6, 120.2, 114.7, 64.4, 62.4, 42.0, 30.9, 14.5, 14.2; LCMS (ESI, *m/z*): Calculated for C₂₁H₂₆N₂O₆ [M+Na]⁺: 425.1683, found- 425.1518.



Tetraisopropyl-1,1'-(propane-2,2-diylbis(6-hydroxy-3,1phenylene))bis(hydrazine-1,2-dicarboxylate)[3b]: The titled compound was prepared following general procedure B in 47% yield [231.69 mg] as colourless oil; eluted in 12% ethyl acetate and hexane (v:v) in silica gel column chromatography; ¹H NMR (500 MHz, CDCl₃): δ 7.08 (d, J = 8.4 Hz, 1H), 6.73 (d, J = 8.4 Hz, 1H), 6.28 (s, 1H), 6.01 (s, 1H), 5.26 (s, 1H), 5.03-4.94 (m, 2H), 1.65 (s, 3H), 1.25 (d, J=7.9 Hz, 12H); ¹³C NMR (126 MHz, CDCl₃): δ 153.8, 152.3, 149.1, 142.2, 127.9, 120.3, 120.1, 114.8, 73.1, 68.6, 42.4, 31.0, 25.3, 21.9; LCMS (ESI, m/z): Calculated for C₃₁H₄₄N₄O₁₀ [M+CH₃CN]⁺: 673.3317, found- 673.3361.

Tetra-tert-butyl 1,1'-(propane-2,2-diylbis-(6-hydroxy-3,1phenylene)) bis (hydrazine-1,2-dicarboxylate)[3c]: The titled compound was prepared following general procedure B in 39% yield [209.39 mg] as white solid; eluted in 10% ethyl acetate and hexane (v:v) in silica gel column chromatography; ¹H NMR (500 MHz, CDCl₃): δ 7.01 (d, J = 8.2 Hz, 1H), 6.68 (d, J = 8.4 Hz, 1H), 6.26 (s, 1H), 6.16 (s, 1H), 6.00 (s, 1H), 1.53 (s, 3H), 1.40 (s, 18 H); ¹³C NMR (126 MHz, CDCl₃): δ 154.7, 153.1, 152.7, 134.1, 126.7, 113.6, 113.5, 80.7, 80.5, 30.0, 28.6, 27.0, 24.3; LCMS (ESI, *m*/*z*): Calculated for C₃₅H₅₂N₄O₁₀ [M-H]: 687.3750, found- 687.3600.



Tetrabenzyl 1,1'-(propane-2,2-diylbis-(6-hydroxy-3,1-phenylene)) bis (hydrazine-1,2-dicarboxylate)[3d]: The titled compound was prepared following general procedure B in 44% yield [282.79 mg] as white oil; eluted in 15% ethyl acetate and hexane (v:v) in silica gel column chromatography; ¹H NMR (500 MHz, CDCl₃): δ 7.40 (dd, *J*= 26.1, 7.6 Hz, 8H), 7.25-7.20 (m, 4H), 7.16-7.12 (m, 8H), 7.08 – 7.05 (t, 2H), 6.71 (d, *J* = 8.5 Hz, 2H), 6.62 (s, 2H), 6.02 (s, 2H), 5.42 (s, 2H), 5.25 (s, 4H),5.16 (s,4H), 1.63 (s, 6H); ¹³C NMR (126 MHz, CDCl₃): δ 156.5, 153.8, 152.2, 149.1, 148.3, 142.2, 135.5, 134.8, 128.6, 127.9, 120.3, 120.1, 114.8, 70.3, 67.9, 42.1, 31.0; LCMS (ESI, *m/z*): Calculated for C₄₇H₄₄N₄O₁₀ [M+Na]⁺: 847.2950, found- 847.2770.



Tetrakis[4-chlorobenzyl]-1,1'-(propane-2,2-diylbis-(6-hydroxy-3,1phenylene))bis (hydrazine-1,2-dicarboxylate)[3e]: The titled compound was prepared following general procedure B in 49% yield [366.91 mg] as white viscous solid; eluted in 10% ethyl acetate and hexane (v:v) in silica gel column chromatography; ¹H NMR (500 MHz, CDCl₃): δ 7.38-7.20 (m, 8H), 7.08-7.05 (m, 8H), 7.06 (d, *J*=2.7 Hz, 4H), 6.72(d, *J*= 2.9 Hz, 2H), 5.21 (s, 8H), 4.90 (s, 2H), 1.66 (s, 6H); ¹³C NMR (126 MHz, CDCl₃): δ 153.7, 153.5, 148.9, 142.5, 134.7, 133.2, 129.9, 128.9, 128.1, 127.9, 120.2, 114.8, 69.4, 42.1, 30.9; LCMS (ESI, *m/z*): Calculated for C₄₇H₄₀Cl₄N₄O₁₀ [M+Cl]⁺: 995.1182, found-995.2161.



Tetrapiperidine-1,1'-(propane-2,2-diylbis-(6-hydroxy-3,1phenylene))bis (hydrazine-1,2-azodicarbonyl[3f]: The titled compound was prepared following general procedure B in 40% yield [228.36 mg] as yellowish oil; eluted in 12% ethyl acetate and hexane (v:v) in silica gel column chromatography; ¹H NMR (500 MHz, CDCl₃): δ 7.84 (s, 1H), 7.19-7.14 (m, 2H), 7.08 (d, *J* = 8.7 Hz, 1H), 6.74 (s, 1H), 3.67 (t, 8H), 3.52 (tt, *J* = 5.4, 5.4, 5.1 Hz, 8H), 1.70 (s, 3H),

1.66-1.58 (m, 4H); ¹³**C NMR** (126 MHz, CDCl₃): δ 161.9, 160.4, 149.0, 148.4, 127.9, 120.9, 120.1, 114.8, 45.4, 44.1, 42.3, 30.5, 25.9, 25.4, 24.1; **LCMS** (ESI, *m/z*): Calculated for C₃₉H₅₆N₈O₆ [M+K]⁺: 771.3954, found- 771.4966.



4-(2-4-hydroxyphenyl)propan-2-yl)-2-(10H-phenoxazin-10-yl)-

phenol[3g]: The titled compound was prepared following general procedure C in 51% yield [162.42 mg] as Greenish solid; eluted in 15% ethyl acetate and hexane (v:v) in silica gel column chromatography; ¹H **NMR** (500 MHz, CDCl₃): δ 7.66 (d, *J* = 7,6 Hz, 2H), 7.25-7.21 (m, 4H), 7.18-7.15 (m, 3H), 7.13-7.04 (m, 4H), 6.71 (d, *J* = 6.7 Hz, 2H), 4.85 (s, 1H), 3.89 (s, 1H), 1.63 (s, 6H); ¹³C NMR (126 MHz, CDCl₃): δ 152.4, 150.8, 149.4, 147.6, 147.4, 141.6, 127.2, 126.9, 126.8, 125.6, 123.8, 122.3, 119.8, 119.3, 115.7, 113.7, 41.0, 29.9; **LCMS** (ESI, *m/z*): Calculated for C₂₇H₂₃NO₃ [M]: 409.1672, found- 409.1510.



4-(2-4-hydroxyphenyl) propan-2-yl)-2-(10H-phenothiazine-10-yl)phenol[3h]: The titled compound was prepared following general procedure C in 63% yield [208.91 mg] as purple solid; eluted in 15% ethyl acetate and hexane (v:v) in silica gel column chromatography; ¹H NMR (500 MHz, CDCl₃): δ 7.53 (d, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 6.9 Hz, 1H), 7.28 (dd, *J* = 8.4,8.2 Hz, 2H), 7.23 – 7.20 (m, 3H), 7.18-7.13 (m, 4H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.70 (d, *J* = 10.0 Hz, 2H), 5.35 (s, 1H), 3.89 (s, 1H), 1.63 (s, 6H); ¹³C NMR (126 MHz, CDCl₃): δ 153.6, 152.2, 149.0, 148.7, 148.3. 137.9, 132.2, 142.3, 129.6, 127.9, 127.6, 126.9, 126.7, 120.9, 120.6, 114.8; **LCMS** (ESI, *m/z*): Calculated for C₂₇H₂₃SNO₂ [M+H]⁺: 425.1444, found- 425.1676.



4-(tert-butyl)-2-(10H-phenothiazine-10-yl)-phenol[3i]: The titled compound was prepared following general procedure C in 44% yield [119.13 mg] as red solid; eluted in 10% ethyl acetate and hexane (v:v) in silica gel column chromatography; ¹H NMR (500 MHz, CDCl₃): δ 7.94-7.90 (m, 2H), 7.63 (d, J = 9.9 Hz, 1H), 7.50-7.45 (dd, J = 6.7, 5.3 Hz 2H), 7.37 (s, 1H), 7.19-7.13 (m, 2H), 7.08 (d, J = 8.7 Hz, 1H), 6.94 (d, J = 6.6 Hz, 2H), 6.76 (s, 1H), 1.25 (s, 9H) ; ¹³C NMR (126 MHz, CDCl₃): δ 146.5, 139.9, 139.2, 135.2, 134.0, 130.9, 127.9, 125.0, 123.7, 120.3, 119.0, 111.8; LCMS (ESI, *m/z*): Calculated for C₂₂H₂₁SNO [M+Cl]⁺: 365.1682, found- 365.1299.

B. PLAUSIBLE REACTION MECHANISM:

• Plausible reaction mechanism for reaction scheme 10:

First the base catalyst transforms the polycarbonate plastic to BPA.



Based on above results of the control experiments and mechanistic study available in literature, the plausible reaction mechanism is outlined. After the formation of bisphenol, irradiation of blue light excites the photocatalyst which oxidizes the phenol and the photocatalyst itself gets reduced. The reduced photocatalyst reduces the azodicarboxylate and O_2 to H_2O_2 , getting back to its neutral position. The H_2O_2 which was formed in-situ leads to the oxidation of Br⁻ ion to hypobromous acid [HOBr]. Then C-N coupling takes place leading to the generation of ortho-aminated product.

• Plausible reaction mechanism for reaction scheme 11:



Figure 14: Plausible reaction mechanism

Based on above results of the control experiments and mechanistic study available in literature, the plausible reaction mechanism is outlined. When the photocatalyst is irradiated with a blue led, it leads to the generation of the excited state of the photocatalyst. The excited photocatalyst can undergo oxidative quenching by $K_2S_2O_8$ by producing radical cation of the photocatalyst and generating SO_4 radical which causes the generation of phenoxide radical through single electron transfer.

Whereas the cation radical of the photocatalyst produces an amine radical from phenothiazine undergoing reductive quenching to its ground state completing the photocatalytic cycle. $K_2S_2O_8$ then enables the formation of a phenoxonium radical intermediate by generating SO_4 -radical. Then a radical-radical cross coupling takes place to furnish a C-N bond between the phenoxonium radical and the amine radical to funish a C-N bond.

C.¹H AND ¹³C NMR SPECTRA:


































A. CONCLUSION:

We have been successful in sustainable transformation of waste CD pellets to bisphenol A which can be further used for polycarbonate plastic production and this is the product found in different everyday use products like shatterproof windows, eyewear, water bottles, lining of canned foods and drinks, many medical devices, helmets, dental sealants etc. It is also used to harden so many plastics and can be used as a flame retardant. Despite all these various applications, it is reported that BPA has some negative hormonal impacts on females.^[19] Therefore, we targeted to synthesize some value- added new product directly from the waste plastic. We have been successful in synthesizing three aminated products using three different azodicarboxylates. The construction of carbon-heteroatom bonds is a crucial transformation for the synthesis of functionalized heterocyclic moieties present in natural products and pharmaceuticals. The aminated products can be used as intermediates for further synthesis of some biologically important compounds.

We have also tried to synthesize some complex compounds having C-N bond following oxidative click coupling approach with cyclic anilines like Phenothiazine, Phenoxazine through the in-situ generation of Bisphenol starting directly from waste plastic material. We have been successful in constructing the aryl C-N bonds through photocatalysis; these aryl C-N bonds are ubiquitous in pharmaceutical, agrochemical and material science. The compounds we have synthesized are showing good absorbance in visible light in contrast to the starting materials which absorb in deep UV region. Therefore, these compounds can show good photochemical properties or can be used as photoinitiator in photocatalysis.

To encapsulate, we can say that all the protocols we have applied for the transformation of waste plastic, don't require any kind of pre-activation of starting material. Moreover, use of any expensive, toxic reagent as well as elevated temperature, harsh reaction condition was also averted.

For our project we have explored mainly three types of waste plastic and ended up getting some value-added products which can further be used for significant purpose. • APPENDIX:

1. NMR data of the Starting Materials:

⁴ ¹H NMR (500 MHz) [In CDCl₃] of Waste CD fragments:







¹H NMR (500 MHz) [In CDCl₃] of Waste Safety glass:

¹³C NMR (500 MHz) [In CDCl₃] of Waste Safety glass :



¹H NMR (500 MHz) [In CDCl₃] of Waste bottle cap:



¹³C NMR (500 MHz) [In CDCl₃] of Waste bottle cap:



Mass Spectrum:

∔ LC-MS data [in MeOH] of [3a]:





LC-MS data [in MeOH] of [3c]:







∔ LC-MS data [in MeOH] of [3e]:



∔ LC-MS data [in MeOH] of [3f]:



∔ LC-MS data [in MeOH] of [3g]:



∔ LC-MS data [in MeOH] of [3h]:



∔ LC-MS data [in MeOH] of [3i]:



IR spectrum of compound [1p]:



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