# Visible Light Induced Photocatalytic Activity of Carbon Nanodots for Important Organic Transformations

Ph.D. Thesis

By Daisy Sarma



# DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE SEPTEMBER 2020

# Visible Light Induced Photocatalytic Activity of Carbon Nanodots for Important Organic Transformations

## A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY

> by DAISY SARMA



# DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE SEPTEMBER 2020



# **INDIAN INSTITUTE OF TECHNOLOGY INDORE**

## **CANDIDATE'S DECLARATION**

I hereby certify that the work which is being presented in the thesis entitled **Visible Light Induced Photocatalytic Activity of Carbon Nanodots for Important Organic Transformations** in the partial fulfillment of the requirements for the award of the degree of **DOCTOR OF PHILOSOPHY** 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, 2015 to September, 2020 under the supervision of Dr. Tridib Kumar Sarma, Assistant professor, Discipline of Chemistry, IIT 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.

Darry Sanma.

Signature of the student with date (Daisy Sarma)

12.05.2021

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

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Inicit W.

12.05.2021

(Dr. Tridib K. Sarma) Thesis Supervisor

# Dedicated to My Motherland

And

My Beloved Family

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#### Abstract

Photochemistry and photocatalysts for the development of green and sustainable pathways have attracted intellectual implementation and resources for applications in diverse areas such as organic conversions, environmental remediation, oxidation or reduction of small molecules ( $CO_2$ ,  $N_2$ ,  $H_2O$  etc.) and energy applications. However, having a clear mechanistic understanding in the photocatalytic processes are often complex and the mechanism vary between various types of catalysts involved.

In this thesis, we have explored the intrinsic photocatalytic activity of carbonaceous nanomaterials namely carbon dots for various important organic transformations such as C-H oxidation, C-C coupling reactions under visible light irradiation. Oxidation of C-H and N-H bonds followed by synthesis of heterocyclic compounds have also been investigated through photocatalytic decomposition of oxidant *tert*-butylhydroperoxide. Further, composite of carbon dots with iron oxide nanoparticle have been explored for cross-dehydrogenative coupling reactions. The catalysts are highly compatible with wide range of substrates. A detailed mechanistic investigation is carried out to understand the role of photocatalysts in catalytic reactions. The thesis is divided into the following chapters.

#### **Chapter 1: Introduction**

In this chapter, a general discussion and literature survey of transition metal based photoredox catalysis and various heterogeneous semiconducting photocatalytic materials including carbonaceous nanomaterials namely carbon dots, their properties, synthesis and their application in chemical reactions have been explained in details.

### Chapter 2: Carboxyl Functionalized Carbon dots as Competent Visible Light Photocatalyst for Aerobic Oxygenation of Alkyl Benzenes: Role of Surface Functionality

In this chapter, we have shown carboxyl functionalized carbon dots as efficient visible light photocatalyst for the C-H oxygenation of alkyl benzene in the presence of *tert*-butyl hydroperoxide (TBHP) as an external oxidant.

Several controlled reactions have been carried out to establish the role of carbon dots in the oxidation reactions. The efficiency of the CDs as photocatalysts for the oxidation reaction was highly dependent on the surface functional groups. In order to compare the activity of surface functional groups on the photocatalytic efficacy of carbon dots for the oxidation of C-H bonds, we also synthesized amine rich CDs (n-CDs) and tested them for C-H oxidation of the model reaction under the optimised reaction condition. Surprisingly, the carboxyl functionalized CDs showed superior photocatalytic efficiency promoting transfer of photoexcited electrons to reactants and favouring inhibition of electron-hole recombination.

#### Chapter 3: Visible-Light Induced Enhancement in Multi-catalytic Activity of Sulfated Carbon dots for Aerobic Carbon-Carbon Bond Formation

In this chapter, we have demonstrated that carbon dots decorated with hydrogensulfate groups can be exploited as a photocatalyst for merging photo oxidation and acid-catalyzed reactions in one pot. We have modified the surface functionalities of the previously synthesized c-CDs with –SO<sub>3</sub>H groups using fuming sulfuric acid. The catalytic activity of as synthesized sulfated carbon dots (s-CDs) were explored towards the C-C coupling reaction of xanthene with ketones, arenes and 1,3-dicarbonyl compounds through a cross dehydrogenative coupling pathway.

A detailed mechanistic investigation was carried out by performing various controlled experiments. The s-CDs demonstrate dual catalytic properties, firstly photoactivation of benzylic  $-CH_2$  groups in xanthene in presence of O<sub>2</sub> resulting in the formation of hydroperoxy intermediate, followed by acid catalyzed coupling with nucleophiles giving final cross-dehydrogenative product.

#### Chapter 4: Photo enhanced decomposition of TBHP: A convenient and greener pathway for aqueous domino synthesis of quinazolinones and quinoxalines

In this chapter, we have shown a simple and environmental-friendly visible light promoted synthetic method for the synthesis of diverse class of N-heterocyclic moieties like quinazolinone and quinoxaline in the presence of *tert*-Butyl hydroperoxide (TBHP) as an external oxidizing agent. Increased rate of decomposition to generate free radicals from TBHP upon visible light irradiation is the driving force for the domino reaction. A wide range of quinazolinones and quinoxaline could be synthesized from easily available starting materials in good to excellent yields in presence of TBHP under visible light irradiation. This methodology that involves no metal or external photocatalysts can be utilized for green synthesis of important bio active molecules through radical chemistry.

### Chapter 5: Carbon Dots Supported Iron Oxide Nanoparticles: An Efficient Magnetically Recoverable Visible Light Mediated Photocatalyst for Cross-Dehydrogenative Coupling Reactions

In this chapter, we have reported CDs stabilized iron oxide NPs as effective magnetically recoverable photocatalyst for cross-dehydrogenative coupling of N-phenyltetrahydroisoquinoline with nucleophiles under visible light irradiation. A cooperativity effect between CDs and  $Fe_3O_4$  were found to be involved during the catalytic reaction. Photoluminescence studies show that there is some electron transfer involved between CDs and  $Fe_3O_4$  which consequently protects the  $Fe_3O_4$  nanoparticles from photocorrosion during photocatalytic process.

Investigation of reaction mechanism suggested involvement of radical species in the reaction pathway, specifically superoxide radicals  $(O_2)$  found to be mainly responsible for the photocatalytic transformations.

#### **Chapter 6: Conclusion and Future Outlook**

This chapter summarizes the works described in the thesis. Further, the relevance and future prospects of the works have been discussed.

#### **Publications (from the thesis):**

- Sarma D., Majumdar B., Sarma T. K. (2019), Visible-Light Induced Enhancement in Multi-catalytic Activity of Sulfated Carbon dots for Aerobic Carbon-Carbon Bond Formation. *Green chemistry*, 21, 6717-6726 (DOI: 10.1039/c9gc02658d).
- Sarma D., Majumdar B., Srama T.K. (2018), Carboxyl functionalized carbon dots as Competent Visible Light Photocatalyst for Aerobic Oxygenation of Alkyl Benzenes: Role of Surface Functionality. ACS Sustainable Chem. Eng., 6, 16573-16585 (DOI:10.1021/acssuschemeng.8b03811).
- Sarma D., Majumdar B., Deori B.; Jain S., Sarma T. K. Photo Enhancement Decomposition of TBHP: A Convenient and Greener Pathway for Aqueous Domino synthesis of Quinazolinones and Quinoxalines ACS Omega (Just Accepted).
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#### **Publications (from non-thesis work):**

- Majumdar B., Mandani S., Bhattacharya T., Sarma D., Sarma T. K. (2017), Probing carbocatalytic activity of carbon nanodots for the synthesis of biologically active dihydro/spiro/glyco quinazolinones and aza-Michael adducts, *J. Org. Chem.*, 82, 2097-2106 (DOI: 10.1021/acs.joc.6b02914).
- Majumdar B., Sarma D., Bhattacharya T., Sarma T. K. (2017), Graphene oxide as metal-free catalyst in oxidative dehydrogenative C-N coupling leading to α-ketoamides: Importance of dual catalytic activity, ACS Sustainable Chem. Eng., 5, 9286-9294 (DOI: assuschemeng.7b02267).
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Functionalization, *Langmuir*, 33, 7622-7632 (DOI: 10.1021/acs.langmu r.7b00557).

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Carboxyl Functionalized Carbon dots as Competent Visible Light Photocatalyst for Aerobic Oxygenation of Alkyl Benzenes: Role of Surface Functionality

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### ACRONYMS

CNT	Carbon nanotubes
CDC	Cross-dehydrogenative coupling
CNDs	Carbon nanodots
GQD	Graphene quantum dots
PL	Photoluminescence
UV-Vis	UV-Visible Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
SAED	Selected area electron diffraction
TEM	Transmission electron microscopy
SEM	Scanning electron microscopy
EDS	Energy dispersive spectrum
HRTEM	High-resolution transmission electron microscopy
PXRD	Powder X-ray Diffraction
FTIR	Fourier Transform Infrared
QY	Quantum yield
AFM	Atomic-force Microscopy
FRET	Forster Resonance Energy Transfer
TCSPC	Time-Correlated Single Photon Counting
NP	Nanoparticle
K <sub>SV</sub>	Stern-Volmer quenching constant
GO	Graphene oxide
AC	Activated carbon
СВ	Carbon black
MRI	Magnetic resonance imaging
EPR	Electron paramagnetic resonance
NMR	Nuclear magnetic resonance
HPLC	High performance liquid chromatography
PPM	Parts per million
BE	Binding energy
TLC	Thin layer chromatography
ICP-AES	Inductively coupled plasma atomic emission
	spectroscopy

TON	Turnover number
RPM	Rotation per minute
TOF	Turnover frequency
PPB	Parts per billion
PEG	Polyethylene glycol
# NOMENCLATURE

λ	Wavelength
nm	Nanometer
π	Pi
eV	Electron-volt
Å	Angstrom
ns	Nanoseconds
М	Molar concentration
μΜ	Micromolar
mM	Millimolar
mg	Milligram
mV	Millivolt
Hz	Hertz
rpm	Revolutions per minute
a.u.	Arbitrary unit
cps	Counts per second
mL	Milliliter
μL	Microliter
μm	Micrometer
°C	Degree Centrigrade
α	Alpha
β	Beta
γ	Gamma

Chapter 1

General Introduction and Background

## 1.1 Introduction

Photochemistry and photocatalysis is the most promising, future-oriented alternatives to address the various environmental problems caused by the consumption of traditional fossil fuels. More than 100 years ago, inspired by the photosynthesis in green plants, pioneer chemist Giacomo Ciamician developed several photochemical reactions using visible light in combination with biochemical or enzyme-catalyzed transformations as features of sustainable chemistry. In the International Congress of Applied Chemistry in 1912, Giacomo Giamicianre affirmed this idea in a famous lecture entitled "*The Photochemistry of the Future*" which is regarded as the first prophecy for the potential of photocatalysis.<sup>[1-2]</sup> During this seminal talk, he pronounced this prophetic sentence:

"On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plains and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is. And if in a distant future the supply of coal becomes completely exhausted, civilization will not be checked by that, for life and civilization will continue as long as the sun shines!"

This event may be considered as the beginning of "green chemistry". A photochemical reaction is capable of producing clean and renewable energy carriers such as hydrogen, methanol or formic acid etc. and also offers a useful alternative to the thermally mediated reactions. In the beginning of the 21<sup>st</sup> Century, photoredox catalysis in organic synthesis has taken a considerable advancement on account of the outstanding contributions from chemist like Alain Deronzier, Ganesh Pandey, Angelo Albini, Janine Cossy, and Frederick Lewis among many others.<sup>[3,4]</sup> Unfortunately the domain did not get expected attention due to the use of the high energetic ultra-violet and far visible range of light, which required special equipment for performing the reactions. However, this perception was changed in 2008, when MacMillan and co-workers exploited photochemically generated radicals to develop an enantioselective alpha-

alkylation of aldehyde using visible light induced photoredox catalyst. This transformation was a milestone leap for the application of visible-light photocatalysts in organic synthesis.<sup>[5]</sup>

# **1.2 Photocatalysis**

For visible light induced organic transformations, the most important factor is the development of photocatalysts that can absorb visible light. As most of the organic molecules are incapable of absorbing visible light themselves, it rely on other light absorbing species which could transform the required light as a input energy source to proceed into the reactions. Typically, a catalytic amount of light absorbing species, such as metal complexes, organic dye molecules or semiconductors materials are used as photocatalysts. For a feasible photocatalytic reaction, the interaction between the excited photocatalyst and substrate molecules is a critical feature. Several terms have been used to define the various mode of photochemical activation. One of the principal modes of action in visible-light photocatalysis is photoinduced electron-transfer (PET) sensitization, popularly known as photoredox catalysis where an electron is transferred to or from substrate which consequently generates anionic, cationic or neutral radicals depending upon the behaviour of the starting materials. Thus typically in a photoredox catalysis process, the photoredox catalyst acts as an initiator of a reactive species by extrusion of a leaving group. In photoredox catalysis, upon irradiation of visible light the excited state of photocatalyst can engage in single electron transfer (SET) with organic substrate to give reactive outer shell intermediates (1 and 2 in fig. 1.1a). These excited state species may act as oxidant and reductant for the substrate in ground state reaction (3 and 4 in fig. 1.1a). Proton-coupled electron transfer (PCET) extends the range of substrates where concerted transfer of a proton and an electron occur (5 and 6 in fig. 1.1b).<sup>[6]</sup> Recently MacMillan and his group explored a strategy by combining a photoredox catalyst with metal or organocatalyst to create a dual or synergistic catalysis platform for integrated C-C bond formation (fig. 1.1c). Through the synergistic catalysis, two activation modes are merged where the transition-metal intermediate trap and stabilize the reactive radical species generated by photoredox steps to make them available for synthesis.<sup>[7]</sup> The most traditional mode of action involved in synthetic photochemical reaction is photosensitization



Photocatalyst

Ni<sup>+1</sup>)

R-R'

R'-X

a) Mechanistic pathways of photoredox catalysis

x

R

R-M(n+3)

X



Figure 1.1. General mechanisms of photoredox catalysis (Adopted from reference 6)

or energy transfer. In photosensitizer electron transferring process, energy is transferred to the substrate which is unable to absorb light at a given wavelength (fig. 1.1d). Most recently there has been several reports on visible-light photocatalysis of UV-absorbing substrates without adding any photocatalysts. In such cases, an electron-donor/acceptor complex is formed *in situ* which has the ability to absorb light at longer wavelength that leads to charge separation (fig. 1.1e).<sup>[8]</sup> Furthermore, photocatalytic reactions are accomplished through photoinduced electron transfer, energy transfer or atom transfer.

## 1.2.1 Homogeneous Photoredox Catalysis

The application of photoredox catalysis in organic synthesis was reported almost 40 years ago. Kellogg, Cano-Yelo and Deronzier demonstrated photoredox catalyzed reduction and oxidation reactions by using transition metal complexes.<sup>[9]</sup> These reports set the foundation of the recent developments in the field of modern photoredox catalysis.

#### **1.2.1.1** Photocatalytic organic transformations by Transition Metals

In last few years there has been significant advances in transition metal based photocatalysts including metal sulphides, inorganic metal oxides, and organometallic complexes. Recently scientists like Macmillan, Yoon and Stephenson have employed several transition metal based photocatalytic systems, particularly ruthenium or iridium polypyridyls in organic transformations owing to their outstanding physical and chemical properties. Simultaneously, other transition metal complexes comprising of chromium<sup>[10-11]</sup>, copper<sup>[12-13]</sup>, zirconium<sup>[14]</sup> and cerium<sup>[15]</sup> are also been reported as effective photocatalysts for various organic transformations.  $Ru(bpy)_3^{+2}$  and related complexes have been widely recognized as visible light photocatalysts,<sup>[16]</sup> for their potential electrochemical and photochemical applications in water splitting,<sup>[17]</sup> CO<sub>2</sub> reduction<sup>[18]</sup> and cataionic polymerizations.<sup>[19]</sup> Upon irradiation of visible light an electron is excited from the metal-centered  $t_{2g}$  orbitals of photocatalyst to a ligand-centered  $\pi^*$  orbital which is termed as metal to ligand charge transfer (MLCT) (fig. 1.2). This results in formation of a reactive species in which metal Ru<sup>II</sup> could be oxidized to Ru<sup>III</sup> and the ligand framework could be reduced via a one electron reduction. Further rapid intersystem crossing (ISC) facilitates the formation of a lower energetic, stable and long lived photoexcited (1.1 µs) triplet MLCT state which in turn could engage in single electron transfer from photocatalyst to reactive substrate by competing with the deactivation pathway.<sup>[20]</sup> Interestingly the redox potential of ruthenium polypyridyl photocatalysts can be tuned by altering the corresponding ligands. Furthermore, the photoexcited species exhibit remarkable enhancement in oxidizing and reducing properties than the ground state species which is beneficial for the initiation of various chemical reactions.

Iridium polypridyl complexes such as fac-Ir(ppy)<sub>3</sub> also have similar MLCT nature and comparable excited state lifetime as that of Ru(bpy)<sub>3</sub><sup>2+</sup> and demonstrate spectacular activity as a photocatalyst.<sup>[9]</sup> Ru, Ir and its analogues have been extensively investigated for the applications in inorganic and materials chemistry such as components of dye-sensitized solar cells<sup>[21]</sup> and organic light-emitting diods<sup>[22]</sup>, initiators of polymerization reactions<sup>[18]</sup> and in photodynamic therapy.<sup>[23]</sup> However, their application in organic synthesis were sporadic till 2008 when Yoon and Macmillan group use Ru(bpy)<sub>3</sub><sup>+2</sup> as a visible light

photoredox catalyst for [2+2] cycloaddition<sup>[24]</sup> and  $\alpha$ -alkylation reaction of aldehydes<sup>[25]</sup> respectively. In recent times a large number of photodriven organic synthesis have been achieved in the presence of ruthenium and iridium as photocatalyst through electron transfer processes.<sup>[19, 9, 26, 27]</sup> Recently, a number



**Figure 1.2.** Molecular orbital depiction of  $Ru(bpy)3^{2+}$  photochemistry (Adopted from reference 19)

of functional groups such as carboxyl,<sup>[28-29]</sup> ethynylbenziodoxolones,<sup>[30-31]</sup> Nhydroxyphthalimide,<sup>[32]</sup> and trifluoroborates<sup>[33]</sup> are employed for new chemical bond construction such as cooper complex Cu(XantPhos)(neo)BF<sub>4</sub> and Cu<sup>I</sup>(phenanthroline)<sub>2</sub> that shows high photocatalytic activity for the synthesis of helical polyaromatic carbocycles<sup>[34]</sup> and atom transfer radical addition (ATRA) reactions<sup>[35]</sup> respectively. In addition chromium and zirconium complexes are also employed for [4+2] cycloaddition reactions<sup>[10-11]</sup> and dibromination reactions.<sup>[14]</sup>

Despite the excellent photophysical properties and wide use in organic synthesis, the metal complex based photocatalysts suffer from intrinsic drawbacks such as high cost, toxicity, recovery or disposal of the metals poses environmental troubles and oxygen and moisture sensitivity which limits their applications for sustainable organic transformations. Therefore, there is a high demand among scientific community of alternative and sustainable pathway for the photodriven organic synthesis.

#### 1.2.1.2 Organic dye molecules as photocatalyst

Presently, organophotocatalysis has received an immense attention due to their low toxicity, low cost and synthetic versatility by employing various organic semiconducting molecules. A range of semiconducting organic molecules have been reported as photocatalysts such as quinoliniums, quinones, xanthenes, cyanoarenes, pyryliums, benzophenones, thiazines acridiniums, in organic synthesis (fig. 1.3).<sup>[36-38]</sup> among which xanthenes and acridiniuims exhibit exceptional absorption properties in the visible range whereas the molecules quinones, benzophenones and cyanoarenes mostly respond in UV region. Cyanoarene molecules have strong electron withdrawing ability which could be exploited to manipulate for the intermolecular [3+2] cycloaddition reaction, oxidation of double bonds to annulation-type adducts, cross-dehydrogenative benzylicamination etc.<sup>[39]</sup> The redox potential of xanthene dyes such as Eosin Y, Rhodamine B, Rose Bengal (RB), rhodamine 6G (Rh6G) lie in the range of several organic molecules which favour the photoinduced electron transfer to substrate molecules. Upon visible light irradiation, dye molecules are activated to its excited, stable triplet state with longer life time through rapid intersystem crossing (ISC) which facilitates the electron transfer from dye molecules to the reactive substrates. These molecules take active part as photocatalyst for oxidative coupling,<sup>[40-41]</sup> reductive coupling,<sup>[42-43]</sup> arylation of diazonium salts<sup>[44-</sup> <sup>46]</sup> etc. Acridiniums and quinoliniums such as 9-mesityl-10- methylacridinium (Mes-Acr<sup>+</sup>) is a fascinating example of organocatalyst with high oxidation potential ( $E_{oxi}$  = 1.88 V). These dye molecules are employed for direct oxidation of cyclic hydrocarbon to corresponding ketone, oxidation of benzene to phenol,<sup>[47-49]</sup> and hydro-trifluoromethylation of olefins.<sup>[50]</sup>

Cyanoarenes **Benzophenone and quinones** NC CN NC NC NC CN CN  $R = H, OCH_3, N(CH_3)_2$ X=O, Sċм CN CN ĊΝ ĊΝ Anthraquinone Fluoreone Acridiniums and Quinolinium  $R_2N$ NR k₁  $R = CH_3, R_1 = H$ R = H, Ph, mesitylR = H, CNXanthenes  $R_3$ COOR  $R_3$ соон  $R_2$ R<sub>3</sub>  $R_2$ HO Ŕ₁ Ŕ₁  $R = R_1 = H$ ,  $R_2 = R_3 = CH_2CH_3$ , Rhodamine B  $R_1 = R_2 = Br, R_3 = H$ , Eosine Y  $R = R_3 = CH_2CH_3$ ,  $R_1 = CH_3$ ,  $R_1 = H$ , Rhodamine 6G  $R_1 = R_2 = I, R_3 = Cl$ , Rose bangal

Figure 1.3. Examples of molecular organic semiconductor-based photocatalysts.

Although transition metal complexes and organic dye molecules show excellent visible light photocatalytic activity for wide range of photoredox transformations, they still suffer from certain disadvantages such as stability in strong acidic or basic reaction medium and presence of strong nucleophiles or electrophiles.<sup>[51]</sup> Most of the metals are usually costly, toxic and O<sub>2</sub> or moisture sensitive which cause a huge storage problem. Further, the photophysical properties of the metal complexes depend extensively on ligands and for high

Chapter 1

activity of the photocatalytic systems, extensive studies are devoted towards molecular design of the organic components and their interaction with the metal ions. Similarly, organic dye molecules are not photostable and degradation of dyes are often reported after extended irradiation with light or with changing of pH of the medium. Dye molecules triarylpyryliums, acridinium quinolinium get deactivated in the presence of several nucleophiles such as phosphates, acetates, amines, or cyanide ions.<sup>[52-54]</sup> The rapid photobleching and decomposition of organic dye by oxidants such as peroxides under irradiation often leads to low yield and selectivity and they also require complex synthetic steps and are difficult to recover.<sup>[55]</sup>

### **1.2.2 Heterogeneous Photocatalysts**

Most of the photocatalytic systems as discussed above are homogeneous in nature and the recovery of the catalyst for another cycle of reaction is a tedious task. From green and sustainable chemistry point of views, development of heterogeneous catalysts that can demonstrate high efficiency over several cycles of organic transformations is a major goal of research. Nanocrystalline semiconducting materials have emerged as promising alternatives to the homogeneous photocatalysts for green chemical pathways with a focus on nontoxicity, biocompatibility, easy recovery and potential recyclability. Understanding the correlation of photophysical activities of the nanocrystals with their photocatalytic activity is critical from both academic and industrial point of views for the development of new sustainable routes for synthesis of fine chemicals. These materials also demonstrate extensive applications in energy, opto-electronic devices as well as decontamination of environmental pollutants.

#### 1.2.2.1 Semiconducting materials as photocatalyst

In 1972, Fujishima and Honda revealed the extraordinary property of TiO<sub>2</sub> towards the photochemical water splitting, and research interests in heterogenous photocatalysis has grown exponentially since then.<sup>[3–5]</sup> Mostly the semiconductor materials such as metal oxides, metal chalcogenides, metal nitrides, metaldichalcogenides functions as promising photoactive heterogeneous photocatalysts.<sup>[56-60]</sup> The photocatalytic efficiency of these materials under light irradiation depends on the band gap (Eg) and band position of the semiconductors. When a metal oxide absorbs light with energy greater than the band gap, the photoexcitation of electrons generate electron-hole pairs (e<sup>-</sup>/h<sup>+</sup>)

(Fig. 1.4). The photoinduced electrons/hole  $(e^{-}/h^{+})$  can act as reductant and oxidant for various organic substrates absorbed on catalyst surface.



Figure 1.4. Mechanism of photocatalysis (Adapted from Reference 58)

For an efficient semiconducting photocatalyst, the band gap position and redox potential plays an important role for the photo-induced electron excitation. The band gap of semiconductor materials varies with their electronic structures. The band gap of a selected semiconductor metal oxides and sulphides is shown in fig. 1.5. Several metal oxides semiconducting materials such as TiO<sub>2</sub>, ZnO, ZrO<sub>2</sub>, NbO<sub>2</sub> etc. have shown excellent photocatalytic activity towards the photodegradation of organic pollutant, hydrogen evolution, waste water treatment etc. TiO<sub>2</sub> is considered as the most promising and extensively explored material as photocatalyst owing to its outstanding optical and electronic properties, low cost, non- toxicity, reusability and chemical stability. The two primary phases of TiO<sub>2</sub>, anatase with band gap 3.2 eV (~ wavelength 388 nm) absorbs light in the UV range and the rutile phase with a band gap of 3.0 eV (~wavelength of 410 nm) absorbs light in the visible range (fig.1.5). The alcohol and amine oxidation were successfully achieved on rutile and Degussa P25 TiO<sub>2</sub> under UV irradiation. However, the low product selectivity discouraged its usage. For practical purposes, photocatalysis using the visible light is much more attractive and several attempts have been made on TiO<sub>2</sub> to extend its light absorption spectral range from UV to the visible region by doping with heteroatoms such as O, N or S as well as metal dopants. Nevertheless, introduction of dopant into bulk TiO<sub>2</sub> causes a decrease in photocatalytic activity under visible light as compared to those formed under UV irradiation.



*Figure1.5.* Band structure of various types of photocatalyst (a) transition metal oxides and (b) transition metal dichalcogenides. (Adopted from reference 61)

#### **1.2.2.2 Plasmonic photocatalysts**

An alternative strategy has been developed to improve the performance of photocatalytic systems by exploring the surface plasmon resonance (SPR) effect of nanostructured Ag, Au and Cu.<sup>[59-60]</sup> Surface plasmon resonance (SPR) is a phenomenon where absorption of light by noble metal nanoparticles takes place as the conducting electrons on their surface undergo collective oscillation induced by the oscillating electric field of the impinging light and the frequency of the incident light photons matches the natural frequency of surface oscillating electrons. As a result of SPR, the spherical noble metal nanoparticles such as Au, Ag or Cu display absorption band at 530 nm, 400 nm and 580 nm respectively and the wavelength of the SPR can be tuned by controlling their size, shape and composition. When these nanoparticles are deposited on a metal oxide surface, electrons below the Fermi level  $(E_f)$  of plasmonic nanoparticle will be excited to the surface plasmon states (SP) leaving the holes below E<sub>f</sub> under visible light irradiation. Further, the electrons in SP state can be injected into the conduction band of the metal oxide which subsequently is converted to an electron acceptor species. The hole (h<sup>+</sup>) would be quenched by the organic substrates to complete

the photocatalytic cycle (Fig. 1.6).<sup>[59]</sup> In such a photocatalytic system, the metal oxide not only acts as a support and shuttle of electron transfer for the plasmonic nanoparticles but can also possess surface acid or base property which facilitates the product formation during heterogeneous reaction process. For the oxidation of alcohols and amines, the loading of Au nanoparticles (>5 nm diameter) on Degussa P25 resulted in an improvement on the product selectivity under visible light irradiation. In addition to TiO<sub>2</sub>, a number of organic transformations have been carried out by a combination of plasmonic nanoparticle with various metal oxides such as ZnO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> etc.<sup>[62-63]</sup>



*Figure 1.6.* Surface plasmonic metal (Ag, Au or Cu) NPs for visible light induced reactions (Adopted from reference 59).

#### 1.2.2.3 Dye sensitized metal oxide photocatalyst

For effective utilization of visible light, various research groups focused on dye sensitized metal oxides in combination with organocatalysts, where the metal oxide nanoparticles are anchored with dye molecules through covalent bonding to make the photocatalytic system heterogeneous in nature. On irradiation of visible light, the organic dye molecules reach an excited state (dye\*). The excited dye molecules inject an electron into the conduction band of metal oxide semiconductor by leaving a positive charge on it to produce Dye<sup>±</sup> free radicals. The injected electrons are finally transferred to an electron acceptor such as O<sub>2</sub>, simultaneously, the dye free radicals drives the transformations of the substrates to desired products through a catalytic cycle of an organocatalyst as illustrated in fig. 1.7.<sup>[59]</sup>

Several other heterogeneous photocatalytic systems based on metal organic frameworks, covalent organic frameworks, metal sulfides, two



Figure 1.7. Dye sensitized photocatalysis (Adopted from reference 59).

dimensional transition metal dichalcogenide (MoS<sub>2</sub>, WS<sub>2</sub>), and semiconducting quantum dots such as CdS, CdSe etc. have been developed to expand the utilization of the solar energy for variety of chemical synthesis.<sup>[64-65]</sup> Two dimensional transition metal dichalcogenides (2D TMD) such as MoS<sub>2</sub>, WS<sub>2</sub> etc. are also excellent photocatalytic materials owing to the high mobility of charge carriers and exceptional optical absorption property.<sup>[66-67]</sup> To take advantage of the interesting layer-dependent enhancement of photoluminescence properties, exfoliation into mono layers is carried out by various exfoliation methods including mechanical exfoliation, chemical exfoliation, ion-intercalation, liquidphase exfoliation and sonication. Solvents with high surface tension such as Nmethyl-pyrrolidone (NMP) or N-vinyl-pyrrolidone (NVP) can be used as exfoliating solvent<sup>68</sup>. The use of strong intercalating agents such as n-butyl lithium napthalenide requires a much longer time for exfoliation (>48 h), sometimes leading to deformation of the original crystal structure of MoS<sub>2</sub>,<sup>69</sup> and post-exfoliation steps are of great challenges for safe and effective scale-up. Again, most of the heterogeneous semiconducting photocatalyst materials are synthesized by the use of toxic metals and the synthetic methods are often tedious. Therefore exploration of low toxic, environmentally friendly and cheap photocatalysts is of high priority to preserve the level of sustainability and wide applications in chemical conversions.

#### 1.2.2.4 Carbon nanomaterials as photocatalysts

Carbon is one of the most abundant elements in nature and plays a unique role in ecosystems and in the human economy. Owing to the diversity in

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structure, tunable porosity, surface chemistry, excellent physicochemical stability, facile synthesis and presence of different active sites, various forms of carbon nanomaterials have been used as catalysts themselves or as a support for other active catalysts. Carbon is present on Earth in living organisms, fixed by photosynthesis, in the form of biomass. This is a readily available-sustainable-source of carbon precursors. Therefore the carbon necessary to make carbon dots is provided by nature, ready to use. On the contrary, metal complexes, metal oxides, organic photocatalysts can only be obtained through long and complex procedures.Various structures and compositions have been developed based on carbonaceous materials through well-designed synthesis strategies to make them effective as photocatalytic systems.

The commonly used carbonaceous materials that have been utilized as catalysts are carbon dots, activated carbon, graphene, g-C<sub>3</sub>N<sub>4</sub>, fullerene, and carbon sponges/aerogels (fig. 1.8). Among the carbocatalyst the activated carbon (AC), activated carbon powder, activated carbon fibers (ACF) are used as adsorbents for various environmental pollution remediation. Carbon catalysts having large surface area and high porosity can lead to synergistic effects with various photocatalysts resulting in enhanced performance.<sup>[70-71]</sup> Semiconducting materials such as TiO<sub>2</sub>, BiVO<sub>4</sub> have been coupled with activated carbon to form composite photocatalysts that increases the activity of photocatalyic degradation of organic pollutant. The research activities for the growth of nanocarbon materials have gained momentum with the development of fullerenes. Although the nanocarbon materials including fullerenes, nanotubes (CNT) and graphene are found to be catalytically active in certain reactions, however these materials alone and without modifications do not display significant photocatalytic activities for either synthesis of fine chemicals or other applications. To make them efficient catalysts the most frequently adopted strategies are doping with heteroatoms, creating defects, and/or forming composites with other semiconducting photocatalysts. The composition of these three allotropes (fullerene, CNT and graphene) with other semiconducting materials improves the photocatalytic activity. The improvement of the activities can be attributed to the fact that addition of carbon contents into the matrix of semiconductors increases the absorption and the life time of the photoexcited electron-hole pairs. In fact the nanocarbon material behaves as an electron reservoir to trap the photoexcited electrons from semiconductors.  $g-C_3N_4$  is a two-dimensional graphene-like layered semiconductor materials comprising of covalently linked  $sp^2$  hybridised carbon, nitrogen and partially hydrogen atoms.  $g-C_3N_4$  exhibit a band gap of 2.7 eV (460 nm) making it a promising visible light candidate for numerous applications such as in solar energy utilization, waste water and environmental



Figure 1.8. Carbonaceous materials for photocatalysts (Adopted from reference 72).

treatment, biomedical and sensing application. Taking advantage of narrow band gap and suitable redox potential,  $g-C_3N_4$  is used for various organic syntheses.

## **1.2.2.4.1** Carbon dots

Fluorescent carbon dots, a new member of carbon nanomaterials with average size less than 10 nm was discovered serendipitously by Xu *et al.* during electrophoretic purification of single walled Carbon nanotubes in 2004.<sup>[73]</sup> In 2006, Sun *et al.* reported the synthesis of fluorescent nanoscale carbon particles via laser abalation of a carbon target and named them as "carbon dots".<sup>[74]</sup> The outer shell of carbon dots consists of oxygen or other heteroatom based functional groups whereas the inner core consists of significant amount of sp<sup>2</sup> hybridized olefinic carbons.<sup>[75]</sup> The basal plane of carbon dots consists of significant amount of sp<sup>2</sup> hybridized carbon atoms along with some oxygen atoms (upto 40%) on the surface due to the presence of carboxyl, hydroxyl, epoxy groups.<sup>[76]</sup> Further, modification of surface can be done simply by doping with N, S, B, P containing precursor molecules for carbonization and controlling the carbonization temperature.<sup>[77-78]</sup> Based on the synthesis methodology the fluorescent nanodots are divided into two categories graphene quantum dots (GQDs) and carbon

nanodots (CNDs). GQD are crystalline in nature with one or a few layers of graphene with lateral dimensions greater than their height. GQD are derived by top-down method by acid hydrolysis of graphene. CNDs are obtained by a bottom-up process by carbonizing carbon based molecules giving quasi-spherical particles with size below 10 nm. By varying the synthetic method, both amorphous or crystalline form of CNDs can be obtained.<sup>[79]</sup>

Unlike other carbon nanomaterials, the most fascinating features of carbon dots is their highly tunable photoluminescence property, the reason why they are also termed as fluorescent tiny dots and carbon nanolights.<sup>[80]</sup> Although the principle of emissive behavior of CNDs are mechanistically not evident, yet it is often assumed that both the surface functional groups and the carbon core play a crucial role to their emission behavior. Nevertheless, the easy synthetic method of carbon dots from easily available cheap carbon source, easy surface modification, photostability, biocompatibility and non-toxicity have made them good candidate with diverse application potential.<sup>[81]</sup> In the last couple of years, significant advancement has been made toward the synthesis, properties and application of carbon dots. Many synthetic methods developed have shown tuning of optical properties by change in shape, size and surface structure of carbon dots.<sup>[82-83]</sup> The inherent photochemical property of CNDs has been explored in energy and catalysis.<sup>[84-85]</sup> The non-toxic, environmentally friendly and biocompatible nature compared to traditional semiconductor quantum dots have shown potential application of CNDs in biosensing and biomedical.<sup>[86]</sup> The change in photoluminescence behavior of CNDs upon interaction with electron donor or acceptor molecules has formed the benchmark of designing of several optical sensors for metal ions, drugs and pollutants etc.<sup>[87]</sup> Moreover, the enzymemimetic activity of CNDs is of advantageous for different biological applications.

#### 1.2.2.4.2 Synthetic strategies for C-dots

The physicochemical properties of carbon nanodots including its crystallinity, size, shape, elemental composition, photoluminescence properties and stability and compatibility mostly depend on the synthetic procedure and the used precursors.<sup>[88]</sup> There are mainly two synthetic approaches for carbon dots synthesis "top-down" or "bottom-up" approaches (fig. 1.9). A top-down approach essentially involves fragmentation of bulky or sheet-like carbon materials such as graphite, carbon fibers, CNT, coal to smaller nanoparticles through chemical,

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electrochemical, or physical approaches. The most commonly used method for synthesis of luminescent carbon dots are oxidizing agents like  $HNO_3$  and  $H_2SO_4$ .<sup>[89]</sup> Hens et al. demonstrated the emission maxima of CNDs depends on the degree of oxidation of the graphitic structure during the oxidation process



*Figure 1.9.Schematic illustration of the two broad categories of C-dots (Adapted from reference 80).* 

using HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> (1:3).<sup>[90]</sup> Wei et al. showed that even CNDs with the same-sizes but different surface charge can exhibit PL from blue to orange.<sup>[91]</sup> CNDs have also been obtained by laser irradiation of carbon powders dispersed in various solvents which were further oxidized and surface passivated to increase the quantum yield.<sup>[92]</sup> However, in the green synthesis of carbon dots, some waste carbon materials such as candle soot, natural gas soot<sup>-</sup> and tire soot are used as the precursors. Most interestingly it is noted that in the green chemistry point of view the top-down method is less popular due to the limitation of the raw materials.<sup>[93]</sup> In bottom-up approach, carbonization of organic biomolecules/polymers results in formation of CNDs. High temperature treatment of organic precursors may give rise to CNDs which has been widely reported.<sup>[94-95]</sup> CNDs have been found to be present in food caramels and instant coffee where the preparation involves heating of carbohydrates and other carbon rich biomolecules.<sup>[97-99]</sup> CNDs are also found to be present in materials available in nature, such as honey and humic acid<sup>.[100-101]</sup> Bottom-up approaches include



**Figure 1.10.** Schematic representation of synthesis of CNDs via top-down and bottom-up approaches and further modification including functionalization, doping and nanohybrid formation (Adapted from reference 96)

alkali/acid-assisted ultrasonic treatment, pyrolytic thermal oxidation, solvothermal treatment and nitric acid reflux oxidation.<sup>[102]</sup> The resulting CNDs are purified by centrifugation, dialysis, electrophoresis or other separation techniques. These approaches typically yield CNDs with surface functional groups and abundant doping states and utilize glucose, citric acid, and amino acids as molecular carbon precursors. Thermal oxidation can be carried out in the presence of air, inert atmosphere, by heating in microwave or autoclaving solutions of the organic precursors. In the formation of carbon dots, usually the organic molecules undergo four stages: condensation, polymerization, carbonization and passivation. Initially the organic molecules through condensation reaction such as amidation,<sup>[103-105]</sup> Aldol condensation,<sup>[106]</sup> Schiff base condensation<sup>[107-108]</sup> and radical reaction forms a chain compound intermediates. In the second stage, the intermediates are further polymerized or aggregates into polymer like carbon dots with certain polymers (also known as carbon clusters) by covalent, non-covalent or other interactions.<sup>[109]</sup> Then in third stage, the polymers carbonizes to form the carbon core, especially at high temperature.<sup>[110–112]</sup> Finally the residual precursors can be modified on the surface of the carbon dots as surface passivating agents to improve the luminescence efficiency. Controlling the carbonization conditions through selection of precursors, properties of resulting CNDs can also be tuned. For example, Wei et al. reported that CNDs resulted from microwave treatment of a solution of glucose and amino acids show varying physicochemical properties with varying

side-chain of amino acid.<sup>[113]</sup> In the green synthesis of CNDs, the "bottom-up" strategy is a widely used mechanism compared to "top-down" synthesis. Through the "bottom-up" approach the most of biomass materials can also be carbonized into c-dots (CDs) at high temperature.

### 1.2.2.4.3 Optical properties of carbon dots

Most of the carbon dots consists of an amorphous to nanocrysalline core with predominantly  $sp^2$  carbon atoms and oxygenated functionalities at their surface unless they are modified doping with other heteroatoms. Carbon dots typically exhibits  $\pi$ - $\pi$ <sup>\*</sup> transition of C=C and n- $\pi$ <sup>\*</sup> transition of C=O with strong light absorption in UV range (200-320 nm) and a tail extending into visible range The most attractive optical property of c-dots is their (fig. 1.11a). photoluminescence which still remains a mystery and debatable (fig. 1.11b). The emission peaks of c-dots are usually wide with large Stokes shift as compared to organic dyes. This broad peak may be a result of the inhomogeneous chemical structure or diverse photoluminescent centers which include surface-located emitters and core-embedded aromatic clusters.<sup>[114]</sup> There are several mechanism available in different literature reports to formulate a unified theory including surface state,<sup>[115-117]</sup> quantum confinement effect<sup>[118–120]</sup> and molecular fluorescence.<sup>[121-122]</sup> The incorporation of oxyfunctionalities on carbon dots surface attributed to the radiative recombination of electrons and holes from the photoinduced charge separation, which are most likely confined/trapped at the surface sites and acted as exciton capture centers. Further, most of the carbon dots possess good photostability i.e. their PL intensity does not bleach upon significant exposure to light. This property stems from the emissive centers of the carbon core.<sup>[75]</sup> C-dots also do not show the property of PL blinking which is commonly seen in dyes, nanocrystal quantum dots, etc.<sup>[76]</sup> Some C-dots have been reported to possess up-conversion fluorescence properties as well.<sup>[123-124]</sup> These outstanding optical properties of c-dots have led to their applications in diverse areas. Carbon dots are reported to be excellent electron donors and acceptors upon photoexcitation.<sup>[125-126]</sup> This property of C-dots has been largely exploited in sensing of molecules and development of visible light photocatalytic system. Although the composites of carbon dots and inorganic materials have shown good photocatalytic performance,<sup>[75-76, 127-128]</sup> there are few reports of carbon dots alone showing photocatalytic activity like the other traditional

semiconductor quantum dots. It is believed that carbon dots merely can also act as visible light photocatalyst since exciton generated on their surface could transfer photogenerated charges for redox reaction. A variety of organic



Figure 1.11. Optical properties of C-dots (adapted from reference 76).

transformations have been explored taking advantage of the tunable optical properties through modification of surface functional groups on the carbon dots surface. Kang *et al.* demonstrated NIR light and visible light driven photocatalytic activity of carbon dots for alcohol oxidation by exploiting their upconversion photoluminescence properties.<sup>[129]</sup> In 2014, the same group reported that the carbon dotscontribution in hydrogen bond catalysis under visible light irradiation.<sup>[130]</sup>

## **1.3 Organization of Thesis**

In this thesis, we have explored the intrinsic photocatalytic activity of carbonaceous nanomaterials namely carbon dots (CDs) for various important organic transformations such as C-H oxidation, C-C coupling reactions under visible light irradiation by exploiting their physicochemical properties and surface properties. Oxidation of C-H and N-H bonds followed by synthesis of heterocyclic compounds has also been investigated through photomediated decomposition of oxidant *tert*-butylhydroperoxide. Further composite of carbon dots with iron oxide nanoparticle have been explored for cross-dehydrogenative coupling reactions. The catalysts are highly compatible with wide range of substrates. A detailed mechanistic investigation is carried out to understand the role of photocatalysts in catalytic reactions.

**Chapter 1** describes the general discussion and literature survey of transition metal based photoredox catalysis and various heterogeneous semiconducting photocatalytic materials including carbonaceous nanomaterials namely carbon dots, their properties, synthesis and their application in chemical reactions have been explained in details.

**Chapter 2** describes the visible light induced photocatalytic activity of carbon dots towards the C-H oxygenation of alkyl benzene in the presence of *tert*-butyl hydroperoxide (TBHP) as an external oxidant. The efficiency of the CDs as photocatalysts for the oxidation reaction was highly dependent on the surface functional groups. The carboxyl functionalized CDs showed superior photocatalytic efficiency promoting transfer of photoexcited electrons to reactants and favouring inhibition of electron-hole recombination.

**Chapter 3** describes that carbon dots decorated with hydrogensulfate groups can be exploited as a photocatalyst for merging photooxidation and acid-catalyzed reactions in one pot. The synthesized sulfated carbon dots (s-CDs) were explored towards the C-C coupling reaction of xanthene with ketones, arenes and 1,3dicarbonyl compounds through a cross coupling dehydrogenative coupling path way. The s-CDs demonstrate dual catalytic properties, firstly photoactivation of benzylic -CH<sub>2</sub> groups in xanthene in presence of  $O_2$  resulting in the formation of hydroperoxy intermediate, followed by acid catalyzed coupling with nucleophiles giving the final cross-dehydrogenative product.

**Chapter 4** describes the visible light promoted synthetic method for the synthesis of diverse class of N-heterocyclic moieties like quinazolinone and quinoxaline in the presence of *tert*-Butyl hydroperoxide (TBHP) as an external oxidizing agent. Increased rate of decomposition generate free radicals from TBHP upon visible light irradiation is the driving force for the domino reaction.

**Chapter 5** describes CDs stabilized iron oxide NPs as effective magnetically recoverable photocatalyst for cross-dehydrogenative coupling of N-phenyltetrahydroisoquinoline with nucleophiles under visible light irradiation. A cooperativity effect between CDs and  $Fe_3O_4$  were found to be involved during the catalytic reaction.

**Chapter 6** describes the relevance of the works done by us as well as their future scope for future application.

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Carboxyl Functionalized Carbon dots as Competent Visible Light Photocatalyst for Aerobic Oxygenation of Alkyl Benzenes: Role of Surface Functionality

### **2.1 Introduction**

Development of a clean, sustainable, and inexpensive methodology for the direct oxidation of Csp<sup>3</sup>-H bonds to obtain corresponding carbonyl compounds has wide prospects in organic synthesis as the oxygenation of inert C-H bond provides a pathway for designing complex structures with applications in pharmaceuticals, functional materials, and agrochemicals.<sup>[1-3]</sup>This C-H oxygenation is commonly achieved using transition-metal-based catalysts which are often expensive, homogeneous, and obtained from limited natural resources.<sup>[4,5]</sup>Several metal-free heterogenic catalytic systems based on graphene, carbon nitride, etc. have also been developed; however, all resulted in poor conversion or required stoichiometric amount of catalysts along with prolonged heating at elevated temperature to afford good conversions.<sup>[6,7]</sup> In recent years, visible light-driven photocatalyzed reactions have opened exciting avenues for important organic transformations, where selective electron and energy transfer to nonabsorbing molecules takes place from light absorbing photocatalysts under milder reaction conditions.<sup>[8,9]</sup>Toward the photooxygenation of benzylic hydrocarbons, organic dyes such as 1,4-dicyanonapthalene, 10-phenyl-9methylacridinium ion, 9-mesityl-10-methylacridinium ion, dicyanopyrazinederived chromophore, 3-cyano-1-methylqui- nolinium ion, and riboflavin tetraacetate as well as metal porphyrins have demonstrated excellent photocatalytic activity.<sup>[10-18]</sup>However, rapid photobleaching of the organic dyes by oxidants such as peroxides under irradiation often leads to low yield and selectivity. Therefore, external additives are often required to improve the photostabilization of the dyes for performing oxidation of challenging substrates. A few metal based heterogeneous photocatalytic systems such as Cr/Ti/Si ternary mixed oxides, Pt/WO<sub>3</sub>, VO@g-C<sub>3</sub>N<sub>4</sub>,<sup>[19-21]</sup> etc. have also been developed for successful oxygenation of C-H bonds. Among the semiconducting quantum dots, cadmium sulphide (CdS) nanoparticles have demonstrated excellent photocatalytic activity for C-H oxidation bond and activation reactions.<sup>[22]</sup>However, several of these methodologies involve use of toxic catalysts, fluorinated solvents, along with ultraviolet light.<sup>[23,24]</sup>Considering the current emphasis on green and sustainable chemistry, identification of metal-free and reusable catalysts for photocatalytic C-H oxidation transformation is highly

desired. Because of the low-cost, biocompatibility, photostability, and facile functionalization, carbon dots (CDs) have emerged as a new class of fluorescent nanomaterials, having wide application potential in bioimaging, sensors, catalysis, drug delivery, and so on. We earlier reported CDs as an effective catalyst for carbon-heteroatom bond formation taking advantage of their acidic surface properties.<sup>[25]</sup> CDs have also been demonstrated as effective near-infrared light driven photocatalysts for oxidation of alcohols to aldehydes.<sup>[26]</sup> Sulfated CDs show photoswitchable acidic behavior, that has been leveraged for ringopening reactions.<sup>[27]</sup> CD composites with metal nanoparticles and metal oxides have been harnessed as photocatalysts for oxidation and activation of C-H bonds.<sup>[28-30]</sup> Recently, Zhang et al. demonstrated good visible light photocatalytic activity of a CD-gC<sub>3</sub>N<sub>4</sub> composite for alcohol oxidation; however, the reaction rates were sluggish for C-H oxidation.<sup>[31]</sup> Various surface functionalities on the unsupported CDs can serve as efficient photoinduced donors or acceptors and promote separation of electrons and holes that can be utilized for photocatalytic organic transformations. This photoenhanced activity of unsupported CDs was realized for aldol condensation.<sup>[32]</sup>However, the photocatalytic activity of unsupported CDs has not been realized for the oxidation of benzvlic hydrocarbons. It is well known that CDs are present in many naturally occurring systems and function as a superb peroxide mimic.<sup>[33,34]</sup>Therefore, we envisioned that photoactivation of CDs might accelerate the decomposition of organic peroxides through electron transfer and stabilize them on the nanoparticle surface. These surface-stabilized radicals are long-lived compared to the solutionbased radicals that might activate the otherwise inert C-H bonds and thus induce oxidation. In this chapter, we describe the development, optimization, and scope of unsupported CDs as visible light photocatalysts for C-H oxidation of alkyl benzenes in the presence of organic peroxides under mild reaction conditions.

### 2.2 Results and discussion

#### 2.2.1 Synthesis and characterization of Carbon dots

The oxygenation of inert C-H bonds in organic substrates under mild reaction conditions is a challenging problem. Therefore, we pursued the activity of unsupported CDs as metal-free photocatalysts for the oxygenation of C-H

bonds in organic substrates. Large-scale synthesis (up to 3 g) of -COOH functionalized CDs (c-CD) could be achieved by carbonization of glucose using oleic acid as a solvent in a microwave reactor (180  $^{\circ}$ C) <sup>[35]</sup> (Figure 2.1a). The CDs thus obtained were readily dispersed in water and was purified by solvent extraction and dialysis (pore size 2 nm). First, the morphology and physicochemical evaluation of the synthesized carbonaceous materials were carried out by various spectroscopic and microscopic techniques. The morphological studies as observed by transmission electron microscopy (TEM) studies showed the formation of quasispherical and fairly monodisperse particles (Figure 2.1b). The particles had a size distribution in the range of 1.5-5 nm (average diameter of 2.3  $\pm$  1.3 nm), calculated from measurement of over a hundred particles (Figure 2.1c). The high resolution TEM image of c-CDs showed the appearance of lattice fringes signifying the (002) lattice of graphitic carbon confirming high crystallinity (Figure 2.1b, inset). The UV-visible spectrum of the aqueous solution showed a peak at 276 nm owing to the  $\pi$ - $\pi$ \* transition of nanocarbon (Figure 2.1d). The c-CD aqueous solution showed excitation-dependent emission properties with the maximum emission at 470 nm upon excitation at 365 nm and the photoluminescence shifted to longer wavelengths with increasing excitation wavelength (Figure 2.1e). Powder X-ray diffraction spectra of c-CDs exhibited a broad peak centered at  $2\theta = 18.1^{\circ}$ , corresponding to a d-spacing of 4.9 Å (Figure 2.1f). The high resolution X-ray photoelectron spectra in the C 1s region of c-CDs revealed the presence of C=C (283.5 eV), C-OH (285.2 eV), -C=O (287.7 eV), and -COOH (288.8 eV) bonds, confirming that the CD surface is decorated with hydroxyl, carbonyl, and carboxylic acid groups (Figure 2.1g). The presence of these functional groups was further supported by the FTIR studies, which showed a broad peak at 3334  $cm^{-1}$ , that can be assigned to the O-H functionality and prominent peaks at 2945 cm<sup>-1</sup> (C-H), 1718 cm<sup>-1</sup> (C=O), 1640 cm<sup>-1</sup> (C=C), and 1030 cm<sup>-1</sup> (C-O-C) (Figure 2.2a). The morphology of the c-CDs were further evaluated by atomic force microscopy (AFM), which showed the presence of particles having sizes in the range of 3-5 nm and topographical heights mostly between 1 and 3 nm (Figure 2.2b). The elemental composition of the c-CDs was further evaluated by elemental analysis (Table 2.1). The total oxygenated functional groups and -COOH groups were quantitatively estimated using the Boehm titration





**Figure 2.1.** (a) Schematic illustration of the preparation process for c-CDs and the purified c-CDs under daylight and 365 nm UV lamp. (b) TEM image of c-CDs, (inset) high resolution image showing the lattice fringes. (c) Histogram for size distribution of c-CDs. (d) UV-Visible spectrum of an aqueous solution of c-CDs. (e) Emission spectra of c-CDs, while excited at variable wavelengths. (f) Powder X-ray diffraction spectra c-CDs showing a broad peak at  $2\theta = 18.1^{\circ}$ . (g) C 1s XPS spectra of c-CDs.

### 2.2.2 Optimization studies and substrate scope

The photocatalytic activity of c-CDs toward C-H oxidation was initially assessed by studying the oxidation of tetralin (1) to tetralone (2), under visible light irradiation (Table 2.2). In the presence of molecular oxygen as the sole oxidant, no conversion takes place. Addition of  $H_2O_2$  as an external oxidant resulted in 40% of 2, however with poor selectivity. In the presence of t-butylhydroperoxide (TBHP) (4 equiv) as external oxidant, the reaction preceded satisfactorily, and full conversion of tetralin with 96% of isolated yield of 2 was obtained with high selectivity (entry 8, Table 2.2). The oxygenation of 1 does not proceed in the dark or under an N<sub>2</sub> atmosphere (entry 9, Table 2.2). Further, no oxidized product



*Figure 2.2.* (a) *FTIR spectra of c-CDs recorded using KBr pellets;* (b) *Atomic force microscopy* (*AFM*) *image of c-CDs deposited on a mica surface.* 

Table 2.1. Elemental analysis of c-CDs

Element	C	Н	0	Adsorbed H <sub>2</sub> O	C/O ratio
Wt % in c-CD	42	6.23	46	5.77	
Atom ratio	3.5	6.225	2.87	0.32	1.21

(2) formation was observed when the reaction was carried out at elevated temperature (100 °C) in absence of visible light, keeping all other conditions similar (entry 10, Table 2.2). Therefore, it can be confirmed that the mere presence of acidic functionality on the c-CD surface in absence of light irradiation does not suffice the oxygenation of the C-H bond, even at elevated temperature. No oxidation took place in the absence of c-CD (entry 1, Table 2.2), indicating that c-CDs acts as active catalysts for the reaction under visible light irradiation and in the presence of oxygen. The solvent screening studies revealed that the reaction took place excellently in a mixture of water and acetonitrile (1:3). Using either pure acetonitrile or water as the solvent resulted in lower yield of the product (5% and 12%, respectively) (entries 12 and 13, Table 2.2). This may be due to low solubility of the organic substrates in water as well as poor dispersibility of c-CDs in acetonitrile. The use of a well-known photocatalyst, eosin Y, resulted in low conversion of the oxidized product (25%, entry 18, Table 2.2). The 2-dimensional carbonaceous counterpart graphene oxide (GO) could

Table 2.2. Optimization of reaction conditions<sup>a</sup>



Entry	Catalyst	Oxidant (eq.)	Solvent	Yield <sup>[b]</sup> (%)	Sel (%)
1	- (hv)	-	H <sub>2</sub> O:ACN	Trace	-
2 <sup>[c]</sup>	$CD(\Delta)$	-	H <sub>2</sub> O:ACN	Trace	-
3	CD (hu)	-	H <sub>2</sub> O:ACN	Trace	-
4	CD (hu)	O <sub>2</sub>	H <sub>2</sub> O:ACN	Trace	-
5	CD (hu)	$H_{2}O_{2}(7)$	H <sub>2</sub> O:ACN	40	70
6	CD (hu)	TBHP(1)	H <sub>2</sub> O:ACN	46	93
7	CD (hu)	TBHP (2)	H <sub>2</sub> O:ACN	70	91
8	CD (hu)	TBHP (4)	H <sub>2</sub> O:ACN	96	99
9 <sup>[d]</sup>	CD (hu)	TBHP (4)	H <sub>2</sub> O:ACN	Trace	-
10 <sup>[c]</sup>	CD (Δ)	TBHP (4)	H <sub>2</sub> O:ACN	Trace	-
11	No (hu)	TBHP (4)	H <sub>2</sub> O:ACN	Trace	-
12	CD (hu)	TBHP (4)	ACN	5	98
13	CD (hu)	TBHP (4)	H <sub>2</sub> O	12	92
14	CD (hu)	TBHP (4)	CH <sub>3</sub> OH	20	95
15	CD (hu)	TBHP (4)	C <sub>2</sub> H <sub>5</sub> OH	23	97
16	GO (hv)	TBHP (4)	H <sub>2</sub> O:ACN	Trace	-
17 <sup>[c]</sup>	GO (Δ)	TBHP (4)	H <sub>2</sub> O:ACN	Trace	-
18	Eosin Y (hu)	TBHP (4)	H <sub>2</sub> O:ACN	25	88
19	rCD (hv)	TBHP (4)	H <sub>2</sub> O:ACN	73	93
20	PCA (hv)	TBHP (4)	H <sub>2</sub> O:ACN	52	70
21	Pyrene (hu)	TBHP (4)	H <sub>2</sub> O:ACN	Trace	-

<sup>*a*</sup>Unless otherwise specified, all the reactions were carried out with 1,2,3,4 Tetrahydronaphthalene (0.5 mmol) as the model substrate; c-CD as catalyst (15 mg); 4 ml of solvent, reaction time 15 h; using 60 Watt white LED lamp (341 W cm<sup>-2</sup>) at 25 °C under aerial conditions; <sup>*b*</sup>isolated yield; <sup>*c*</sup>reactions performed under dark condition at 100 °C, <sup>*d*</sup>under N<sub>2</sub> environment.

not catalyze the oxidation reaction even at elevated temperatures (entries 16, 17 Table 2.2). Reduced c-CDs (r-CD), which were obtained by reduction of the c-CDs using NaBH<sub>4</sub>, could catalyze the reaction only with lower conversion (73% entry 19, Table 2.2). For comparison, we also studied the photocatalytic activity of a  $\pi$ -conjugated system, 1-pyrene- carboxylic acid (PCA) as a model catalyst, which resulted in significant conversion (52%, entry 20, Table 2.2) under visible light irradiation, on the other hand use of pyrene as a photocatalyst afforded negligible formation of the oxidized product (entry 21, Table 2.2).

With the optimal reaction conditions in hand, we subsequently investigated the substrate scope for C-H bond oxidation (Table 2.3). The photocatalytic oxidation of tetralin and Indan gives their corresponding ketones in excellent yields (entries 1 and 2, Table 2.3). Diphenylmethane and its methoxy substituent afford corresponding benzophenone with high yield (entries 3a, 4a, Table 2.3). Among polycyclic aromatic hydrocarbons, where 9H-fluorene could be converted to 9-fluorenone with a moderate yield (65%), acenaphthene afforded a mixture of ketone and alcohol (entries 5a-6a, Table 2.3). 2-Ethylnaphthalene could be efficiently oxidized to form 2-acetonapthone (entry 7a, Table 2.3). An exception was the case of 9,10-dihydroanthracene, where the dehydrogenation product was favoured over the oxidation product (entry 8a, Table 2.3), since the dehydrogenation products are more stable compared to their corresponding oxidized products. Xanthene and their substituents afforded their corresponding keto products with high yield and selectivity (Entry 9a-12a, Table 2.3). Interestingly, visible light-driven oxidation of isochroman resulted in the formation of isochromanol as the major product (entry 13a, Table 2.3). The oxidation of cyclohexane was found to be sluggish and resulted in very low conversion under similar reaction conditions, even after prolonged reaction time (entry 14a, Table 2.3). It is important to note that N-heterocyclic compounds with pyridinic skeleton such as 3-methylpyridine and 3-ethylpyridine could be converted to the corresponding ketones with much lower yield using the present method (entries 15a, 16a Table 2.3). This could be attributed to the passivation of the photocatalytically active surface traps on the c-CD surface by pyridinic moiety. Photocatalytic treatment of 1,2,3,4-tetrahydroisoquinoline led to the formation of isoquinoline with excellent yield (entry 17a, Table 2.3).

Further, we extended the methodology for the oxidation of benzyl alcohols. c-CDs showed efficient photocatalytic efficiency for the conversion of benzyl alcohols to their corresponding aldehydes with high selectivity in the presence of TBHP as the external oxidant under mild reaction conditions. (Table 2.4).

Substrate	Product	Time (h)	$\begin{array}{c} \text{Yield}^b \\ (\%) \end{array}$	Sel. (%)	Entry
	O C	12	96	99	1a
	°	12	89	95	2a
		15	82	93	3a
		15	76	95	4a
	° C	20	65	97	5a
	O OH	20	82	82/17	6a/6a <sup>/</sup>
		15	73	98	7a
		10	88	22/78	8a/8a <sup>/</sup>
		16	79	96	9a

Table 2.3. Substrate scope of the photocatalytic C-H oxidation of benzylic hydrocarbons<sup>a</sup>

	e				
		15	82	94	10a
ОН	O O O O O O O H	8	85	95	11a
CI OCI	O O CI	10	83	96	12a
0	OH OH	12	74	98	13a
$\bigcirc$	O U	24	9	97	14a
N	O H N	24	25	97	15a
N	O N N	24	33	96	16a
N <sub>H</sub>	N	12	85	91	17a

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<sup>*a*</sup>Unless specified otherwise, all the reactions were carried out with substrate (0.5 mmol), c-CD photocatalyst (15 mg), solvents  $H_2O:ACN = 1:3$  (total 4.0 mL), 4.0 eq. TBHP, using 60 W white LED lamp (341 W cm<sup>-2</sup>) at 25 °C under aerial conditions. <sup>*b*</sup>Isolated yield.

It is interesting to note that, in absence of light, c-CDs could catalyze the oxidation of benzyl alcohol with low conversion (35%) and poor selectivity (72%) to benzaldehyde (entry 2b, Table 2.4). Substituted benzyl alcohols, both with electron-donating and electron-withdrawing substituents, could be converted efficiently to their corresponding aldehyde products at room temperature.

Substrate	Product	$\operatorname{Conv}^{b}(\%)$	Yield <sup>c</sup>	Sel.(%)	Entry
			(%)		
ОН	O H	>99	82	99	1b
ОН	O H	35	21	72	<sup>d</sup> 2b
СІ	CI H	>99	82	97	3b
F	F H	>99	92	95	4b
Br	Br H	>99	88	99	5b
Ме	Me	`H >99	78	98	6b

#### Table 2.4. Oxidation of benzylic alcohols<sup>a</sup>

<sup>a</sup>Unless specified otherwise, all the reactions were carried out with alcohol substrate (0.5 mmol), c-CD catalyst (15 mg), 4.0 eq. TBHP, solvents  $H_2O$ :ACN = 1:3 (total 4.0 mL) Time =7 h, using 60 W white LED lamp (341 W cm<sup>-2</sup>) at 25 °C under aerial conditions. <sup>b</sup>Determined by <sup>1</sup>H NMR. <sup>c</sup>Isolated yield. <sup>d</sup>Reaction performed in absence of visible light irradiation.

### 2.2.3 Recovery and Recyclability

In order to further evaluate the participation of c-CDs in the catalytic reaction, the model C-H oxidation reaction was stopped after 50% conversion, and c-CDs were removed from the reaction mixture by centrifugation. The reaction was continued with the supernatant under visible light; however, no further oxidized product was formed (Figure 2.3a). Additionally, the progress of the reaction was monitored by turning off the visible light source from time to

time. Negligible progress in the formation of the oxidized product was observed in the dark (Figure 2.3b). These results confirmed that the photocatalytic process occurred on the c-CD surface. c-CDs are highly dispersed in water and they can be reused directly after the oxidized products are extracted in organic phase without any treatment. The recyclability of these photocatalysts was studied by monitoring the model reaction over three cycles. The repeating experiments for the model reaction demonstrated that c-CDs could retain over 84% catalytic activity after the third cycle without loss of selectivity (Figure 2.3c).



**Figure 2.3.** (a) Photocatalytic conversion of tetralin to tetralone as a function of time under visible-light irradiation using 60 W white LED lamp at 25 °C in the presence of c-CDs as photocatalyst (blue line) and after removal of the c-CDs after 6 h (red line); (b) Progress of the photooxidation of tetralin under visible-light irradiation (green) and in dark condition (red) under the optimized reaction conditions. The lamp was turned off from time to time and the formation of the desired product tetralone was monitored using a GC instrument; (c) Recyclability test for monitoring the efficiency of c-CDs as a photocatalyst for the C-H oxidation in a cycle of reactions.

TEM study of the recovered c-CDs after the third cycle of reaction did not show pronounced morphological changes (Figure 2.4a). However, we observed a minor blue shift in the emission peak as well as increase in the fluorescence

intensity in the recovered c-CDs compared to the pristine ones (Figure 2.4b). This suggests a partial reduction of the surface functional groups.<sup>[37]</sup> Time-correlated single-photon counting (TCSPC) measurements show that the average fluorescence lifetime of the recovered c-CDs enhanced to 2.4 ns as compared to the pristine c-CDs (1.5 ns) (Figure 2.4c). X-ray photoelectron spectroscopy showed an increase in carbon content in the recovered catalysts with an increase in C/O ratio from 0.663 to 0.698 (Figure 2.4d). In the high resolution C1s core level XPS spectra of recovered CDs, the relative intensities of the functional groups were found to be transformed as compared to c-CD (Figure 2.4e). There was an increase in the graphitic content as compared to oxygen functionalities, suggesting the possible reduction of carboxylic acid groups during the photocatalytic reaction. This is also supported by elemental analysis (Table 2.6). IR spectroscopy further supports the possible reduction in the oxygenated functionality of the recovered c-CDs as indicated by significant reduction in the band at 1715 cm<sup>-1</sup>, associated with C-O stretching of carbonyls and 1030 cm<sup>-1</sup> corresponding to C-O-C stretching (Figure 2.4f). Further, we performed the quantitative determination of the hydroxyl and carboxyl functional groups of the recovered c-CDs after the third cycle using the Boehm titration method, where the ratio of -COOH: -OH functional groups were found to be 1:11.8. The results suggested that the acidic functionality on the CD surface was slightly reduced during the catalytic reaction.

In order to compare the activity of surface functional groups on the photocatalytic efficacy of carbon dots for the oxidation of C-H bonds, we also synthesize amine rich CDs (n-CDs). A similar synthetic method was adopted as that for the c-CDs, where a mixture of glucose and urea (glucose: urea molar ratio is 1:1) were carbonized at 180 °C in a microwave reactor using oleic acid as a solvent. The n-CDs showed two distinct bands at 244 nm and 343 nm which can be assigned to the  $\pi$ - $\pi$ \* transition of the aromatic sp<sup>2</sup> domain and n- $\pi$ \* transition of sp<sup>3</sup> clusters respectively (Figure 2.5a). The n-CDs showed excitation wavelength dependent emission properties, with the maximum emission at 537 nm while excited at 380 nm (Figure 2.5b). The FTIR spectra of n-CDs showed a broad band in the range of 3000-3500 cm<sup>-1</sup> that can be assigned to stretching vibrations of -OH and -NH<sub>2</sub> groups. Further the appearance of strong bands at

1662 cm<sup>-1</sup> (C=O stretching) and at 1567 cm<sup>-1</sup> that can be assigned to N-H stretching, shows that the n-CD surface is decorated with both -COOH and  $-NH_2$  functional groups (Figure 2.5c).



**Figure 2.4.** (a) TEM image of CDs recovered after the third cycle; (b) Fluorescence emission spectra of the pristine and recovered c-CDs; (inset) normalized spectra; (c) Lifetime decay of pristine c-CDs and recovered c-CDs after  $3^{rd}$  cycle; (d) XPS survey spectra of the c-CD and recovered c-CDs; (e) C 1s spectra of c-CDs recovered after the  $3^{rd}$  cycle; (f) FTIR spectra of c-CDs and recovered c-CDs after 3rd cycle of reactions.

Table 2.5. Fluorescence lifetime

Sample	$\tau_1$ (ns)	a1	$\tau_2$ (ns)	a2	$\tau_{avg}$ (ns)	c
c-CD	0.68	0.64	3.16	0.36	1.5	1.3
Recycled CD	1	0.55	4.2	0.45	2.44	1.1

**Table 2.6.** Elemental analysis of the c-CDs recovered after the  $3^{rd}$  cycle

Element	С	Н	0	Adsorbed H <sub>2</sub> O	C/O ratio
Wt% in recycled c-CD	44	2.84	44	9.16	
Atom ratio	3.66	2.81	3.66	0.51	1

Transmission electron microscopy (TEM) studies showed the formation

of quasispherical and uniformly dispersed particles (Figure 2.5d), having an average dimension of  $3.1 \pm 0.8$  nm (Figure 2.5e).



Figure 2.5. (a) UV-visible spectra of n-CDs in water; (b) Excitation wavelength dependent emission spectra of n-CDs; (c) FTIR spectra of n-CDs recorded using KBr pellets; (d) TEM image of n-CDs; (e) Particle size distribution.

Table 2.7. Photocatalytic C-H Oxidat	tion of Benzylic Hy	$vdrocarbon\ catalyzed\ by\ n-CD^a$
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Entry	Substrate	Product	Time (h)	$\begin{array}{c} \operatorname{Conv}^b \\ (\%) \end{array}$	Yield <sup>c</sup> (%)	Sel. (%)
1		0 C	15	86	62	93
2		0 I I I I I I I I I I I I I I I I I I I	20	75	46	88
3			20	84	38	95
4			20	98	59	90

<sup>a</sup>Unless specified otherwise, all the reactions were carried out with substrate (0.5 mmol); n-CD Catalyst (15 mg); 4.0 equiv ,TBHP, solvents  $H_2O$ :ACN = 1:3 (total 4.0 mL) using 60 W white LED lamp (341 W cm<sup>-2</sup>) at 25 °C under aerial conditions, <sup>b</sup>Determined by <sup>1</sup>H NMR, <sup>c</sup>Isolated yield.

The photocatalytic activity of the n-CDs for C-H oxidation was

examined for the model substrate tetralin maintaining the similar optimal reaction conditions, as used for c-CDs. In the presence of 4.0 equiv of TBHP, tetralone was obtained with 62% isolated yield, under visible light irradiation for 15 h at 25 °C. The results suggested that n-CDs showed significantly lower catalytic activity for the C-H oxidation in comparison to c-CDs, signifying that the presence of amine functionality on the carbon dot surface had a detrimental effect on photocatalytic activity. The C-H photocatalytic oxidation reaction was also carried out for a few other substrates, all of which showed significantly lower yield of the oxidized products as compared to c-CDs and even r-CDs (Table 2.7).

#### 2.2.4. Mechanistic Investigation

In order to understand the role of photogenerated radical intermediates and underlying reaction mechanism involved in the TBHP mediated c-CD catalyzed C-H oxygenation, we performed a series of control experiments for the model oxidation reaction (Figure 2.6). The photocatalytic activity was completely inhibited in the presence of a radical scavenger, butylated hydroxytoluene (BHT) indicating that the reaction involved radical species.<sup>[38]</sup> When an 'OH radical scavenger, *tert*-butyl alcohol (TBA) was added, no effect on the conversion was observed. Similarly, *p*-benzoquinone (BQ) as an 'O<sub>2</sub>' scavenger had no impact in the reaction. The results suggest that the oxidation of the C-H bonds in the present system could not be associated with 'OH or 'O<sub>2</sub>' radicals. When 2,2',6,6'tetramethylpiperidine N-oxyl (TEMPO), a highly selective scavenger for carbon centered radical, was added to the photocatalytic reaction, reduced conversion (34%) was observed. This suggests that carbon centered radicals are involved as reactive species during the photochemical reaction.



**Figure 2.6.** Control experiments of photocatalytic C-H oxidation of tetralin with the addition of various radical scavengers: butylated hydroxytoluene (BHT), p-benzoquinone (BQ,  $O^2$ -scavenger), tert-butyl alcohol (TBA, OH radical scavenger), 2,2',6,6'-tetramethylpiperidine N-oxyl (0.12 mmol of TEMPO, carbon centered radical scavenger), EDTA-2Na (hole scavenger) and AgNO<sub>3</sub> (electron scavenger).

Further, the addition of EDTA-2Na as a hole (h<sup>+</sup>) scavenger or AgNO<sub>3</sub> as an electron (e<sup>-</sup>) scavenger completely inhibited the reaction and no conversion of tetralin was observed in either cases.<sup>[39]</sup> The results suggest that the generation of the electron-hole pair in c-CDs upon visible light illumination is crucial for the observed photocatalytic activity.

The transient photocurrent experiment further revealed the formation of  $e^-$ /h<sup>+</sup> pairs upon visible light irradiation (Figure 2.7). Irradiation with visible light causes a rapid increase in the intensity of the photocurrent and returned to zero when irradiation was discontinued. The high photocurrent response is indicative of the highly efficient separation of  $e^-$  and  $h^+$  contributing to high photocatalytic efficiency.



Figure 2.7. Transient photocurrent response of c-CDs under visible light.

To further understand the electron transfer process, Kubelka-Munk-transformed reflectance spectrum of c-CD was used to evaluate the optical band gap, which was calculated to be 2.53 eV. Cyclic-voltammetry experiments revealed thelowest unoccupied molecular orbital (LUMO) of c-CD at  $E_{red/onset}$ = -0.24 V vs Hg/HgCl<sub>2</sub> (Figure 2.8). The corresponding HOMO level was estimated by subtracting the LUMO level from the optical band gap and a value of +2.77V indicates a high oxidizing nature of c-CD.

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**Figure 2.8.** a) Band gap of c-CD obtained obtained from UV-Visible spectrum and calculated using Kubelka–Munk theory; b) Reduction potential of c-CD measured by cyclic voltammetry; c) HOMO/LUMO band positions of c-CD; d) Cyclic voltamograms of the c-CDs/ITO electrode in acetonitrile using lithium perchlorate (LiClO<sub>4</sub>) as an electrolyte under visible light irradiation or without light irradiation.

Further insights into the role of c-CDs in the reaction mechanism came from electron paramagnetic resonance (EPR) studies. The c-CDs show a narrow EPR signal at g = 2.0051 under visible light irradiation. This signifies the singly occupied orbital in ground state c-CDs and indicates that the c-CDs could act as electron donors or electron acceptors during reaction.<sup>[40-41]</sup> Upon TBHP addition, the EPR signal of the c-CDs disappeared due to the decreased number of unpaired electrons, demonstrating electron transfer between c-CDs and TBHP (Figure 2.9a). The photoinduced electron transfer properties of c-CDs were confirmed by observing the emission quenching in presence of either electron acceptor or electron donor molecules in solution under visible light irradiation.

When known electron acceptors 2,4-dinitrotoluene (DNT, 0.9 V vs NHE) or electron donor *N*,*N*-diethylaniline (DEA, 0.88 V vs NHE) were added to the c-

CD aqueous solution, its emission intensity at 470 nm was efficiently quenched. The Stern-Volmer quenching constants (Ksv=  $\tau_F^{\circ}kq$ ) were calculated from the linear regression and found to be 0.484 mM<sup>-1</sup> and 2.45 M<sup>-1</sup> for DNT and DEA respectively (Figure 2.10a, b). Additional evidence for the photoinduced electron transfer from c-CDs was obtained from fluorescence spectral studies, when we observed an efficient quenching of emission intensity of c-CDs with time in the presence of TBHP and visible light (Figure 2.9b). The Stern-Volmer quenching constants (Ksv =  $\tau_F^{\circ}kq$ ) were evaluated from linear regression (Figure 2.9c). It is worth mentioning that c-CDs were fairly photostable under visible light irradiation in the absence of TBHP (Figure 2.10c). Time-resolved fluorescence measurements also showed a continuous decrease in the average lifetime of c-CDs with time in the presence of TBHP (Figure 2.9d). The observations suggest that the photogenerated charge transfer from the surface of c-CDs to TBHP results in the formation of holes as well as decomposition of TBHP into free radicals, that is instrumental in effective C-H oxidation.



**Figure 2.9.** (a) EPR signal for c-CDs and TBHP treated c-CDs; (b) Time-dependent fluorescence quenching of c-CDs in the presence of TBHP and visible light demonstrating efficient electron transfer from c-CD to TBHP; (c) Steady state Stern–Volmer plot for the quenching of c-CD fluorescence at various concentrations of TBHP (excitation at 507 nm); (d) Lifetime decay curves

of c-CDs on addition of TBHP at different time intervals under visible light illumination.



**Figure 2.10.** Stern–Volmer plots for the quenching of luminescence quantum yields (454 nm excitation) of the CDs by (a) 2,4-dinitrotoluene in tolune, (b) DEA in methanol, (c) Photostability study of c-CDs under visible light illumination. The emission intensity of c-CDs was measured under 60 W light illumination with time.

Table 2.8. Fluorescence lifetime

Sample	$\tau_1$ (ns)	a1	$\tau_2$ (ns)	a2	$\tau_{avg} (ns)$	С
CD (0 min)	0.687	0.65	3.03	0.35	1.5	1.02
CD (30 min)	0.644	0.7	3.01	0.3	1.35	1.05
CD (60 min)	0.640	0.66	2.75	0.33	1.32	1.27
CD (180 min)	0.580	0.73	3	0.27	1.23	1.27

It is well known that during semiconductor photoexcitation, effective separation of electron-hole pairs induces faster carrier migration that controls their photocatalytic activity.<sup>[42]</sup> Further, the ligand shell composition is known to influence the photocatalytic activity of semiconductor nanoparticles such as CdS.<sup>[43]</sup> In case of CDs, although the emission mechanism is not clearly understood, it is widely accepted that oxygenated functionalities such as -C=O

and -COOH can introduce trapping states with different energy levels showing semiconductor like properties,<sup>[44]</sup> that contribute to the excitation dependent emission behaviour. To further verify the role of carboxy functionality on CDs surface, we treated the c-CDs with 2M of NaOH solution (c-CD<sub>NaOH</sub>) as base treatment of graphite oxide materials are known to deprotonate the acid functionalities.<sup>[40,45]</sup> FTIR studies of c-CD<sub>NaOH</sub> showed that the intensity owing to the -COOH band in c-CD decreased significantly due to deprotonation of the-COOH group (1715 cm<sup>-1</sup>), while the relative intensity of the sp<sup>2</sup> C=C band at 1639 cm<sup>-1</sup> enhanced significantly (Figure 2.11). When the model C-H oxidation reaction was carried out using c-CD<sub>NaOH</sub> as the photocatalyst, the desired product tetralone was obtained with significantly lesser yield (41%) under the optimal reaction conditions. These studies have clearly demonstrated that the photocatalytic efficacy of c-CDs for the C-H photooxidation reaction was largely affected by the surface states.



Figure 2.11. FTIR spectra of c-CD (blue) and c-CD <sub>NaOH</sub> (red).

In the photocatalytic reaction, usually the efficiency (Q) is highly dependent on the sum of rate of charge transfer from the c-CDs  $(k_{et})$  and the electron-hole recombination  $(k_r)$  (equation 1).<sup>[46]</sup>

$$Q = k_{\rm et}/(k_{\rm et} + k_{\rm r}) \tag{1}$$

The efficiency Q is related to length (D) of the depletion layer, a charge

region that causes an increase of hole carriers and decrease in electron carriers, as in (equation 2)  $^{[47-48]}$ 

$$D = (Q/a) + L (Q-1)$$
(2)

where *a* is the reciprocal absorption length and *L* is the minority carrier diffusion length and can be correlated to  $k_r$  and  $k_{et}$  by equation 3:

$$k_r = k_{\rm et} (1 - aD)/(aD + La) \tag{3}$$

Therefore, a broad depletion layer and high upward broad bending can result in low electron-hole recombination. In the case of c-CDs, the surface is decorated with -COOH functionalities in solution inducing high upward band bending, thus enhancing the hole mediated photocatalytic process. These functional groups can provide an internal electric field by band modulation facilitating effective separation of the electron-hole pairs, thus inducing faster migration of holes to the surface.<sup>[49-51]</sup> In the case of -C=O and -COOH functionalized c-CD, low emission intensity indicates a low recombination rate for the photoinduced e<sup>-</sup>/h<sup>+</sup> pairs, thus inducing effective hole transportation toward surface. In the case of amine functionalized CD (n-CDs) as a photocatalyst, the presence of amine groups induce surface passivation leading to enhancement in emission intensity.<sup>[52]</sup> As expected, n-CDs turned out to be less effective for oxidation as a photocatalyst as compared to c-CDs. Further, the photocatalytic activity of partially reduced CDs (r-CDs) decreased significantly as compared to c-CDs, although the emission intensities were enhanced upon reduction.



Figure 2.12. a) Fluorescence emission spectra of the pristine c-CD and r-CDs; (inset) normalized

spectra; b) Lifetime decay of pristine c-CDs, r-CD and n-CDs.

The r-CDs contain more -OH surface functionality compared to c-CDs, which induce low upward band bending decreasing the hole-mediated process and facilitate electron-hole recombination, as reflected by their enhancement in emission and increase in lifetime (Figure 2.12a,b)

 Table 2.9. Fluorescence lifetime

Sample	$\tau_1$ (ns)	a <sub>1</sub>	$\tau_2$ (ns)	a <sub>2</sub>	$\tau_3$ (ns)	a <sub>3</sub>	$\tau_{avg} (ns)$	c
c-CD	0.68	0.64	3.16	0.36	0	0	1.5	1.3
r- CD	1.19	0.65	5.17	0.35	0	0	2.6	1.1
n-CD	0.33	4.5	15	0.36	0.89	0.31	7.18	1.04

Based on the experimental results and control experiments, the following photocatalytic mechanism for the C-H bond oxidation is proposed (Scheme 2.1). Upon visible light irradiation, excitation of electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) in c-CDs generates reductive electrons and oxidative holes. Effective electron transfer from c-CDs to t-BuOOH results in the formation of alkoxy radicals t-BuO' and OH' radical. The nanoparticle surface can stabilize the reactive radical species generated from the decomposition of TBHP through their defects or holes, resulting in better photocatalytic activity.<sup>[53]</sup> The surfacestabilized radicals abstract one of the hydrogen atoms from hydrocarbons to produce alkyl radical intermediate. The radical intermediate then reacts with O<sub>2</sub> (atmospheric or in situ generated)<sup>[54-55]</sup> to form alkyl peroxy derivatives, which finally undergoes auto oxidation to give the desired oxidation product. The involvement of the alkyl peroxy derivative as an intermediate was confirmed through isolation and NMR/HRMS study during the oxidation of 2methoxyxanthene. The  $\pi$ - $\pi$  interaction between CDs and hydrocarbons might be beneficial to the enrichment of the organic substrates for the promotion of surface-catalyzed organic transformations. The function of the -C=O and -COOH groups on the c-CD surface are similar to the other photocatalytic systems that



facilitates effective electron-hole separation and faster carrier migration.

*Scheme 2.1.* Proposed mechanism for the photooxidation of benzylic hydrocarbon using c-CD as photocatalyst in presence of TBHP.

### **2.3 Conclusions**

In summary, fluorescent carbon dots coupled with TBHP affords a readily accessible, inexpensive, and recyclable catalytic system for the visible-light driven aerobic C-H oxidation of alkyl benzenes. The efficiency of the CDs as a photocatalysts for the oxidation reaction was highly dependent on the surface functional groups. The carboxyl functionalized CDs showed the best photocatalytic efficiency promoting transfer of photoexcited electrons to reactants and favoring the inhibition of the electron-hole recombination. Photoinduced electron transfer from CDs to TBHP resulted in the generation of alkoxy radicals, which could be stabilized for longer durations on the nanoparticle surface. A detailed mechanistic investigation into the parameters controlling the photocatalytic activity of carbon dots is critical for their applications in a wider range of organic transformations.

### 2.4 Experimental Section

#### **2.4.1 General Information**

The powder XRD measurements were carried out by using a Bruker D8

Advance X-ray diffractometer with CuK $\alpha$  source (wavelength= 0.154 nm). TEM images were obtained by using a JEOL JEM- 2100 microscope operated at 200 kV. Atomic force microscopy was carried out by using an AIST-NT instrument (model SMART SPM 10000, Tapping mode), the samples were prepared by drop casting a water dispersion on mica. FTIR spectra were recorded with KBr pellets by using a Bruker Tensor 27 instrument. UV-visible measurements were performed using a Varian Cary 100 Bio spectrophotometer. Emission spectra were taken in a fluoromax-4p fluorimeter from HoribaYovin (model: FM-100). The samples were excited at different excitation wavelength ranging from 310 to 520 nm. The time resolved fluorescence studies was performed on Horiba Yovin (model: Fluorocube-01-NL), a nanosecond time correlated single photon counting (TCSPC) system. X-ray photoelectron spectra (XPS) were recorded using an ESCA instrument, VSW of UK make. EPR measurements were carried out using a JEOL spectrometer (Model: JES-FA200). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with Bruker Advance (III) 400 MHz or 100 MHz spectrometers, respectively. Data for <sup>1</sup>H NMR spectra are reported as chemical shift ( $\delta$  ppm), multiplicity (s=singlet, d = doublet, t = triplet, m = multiplet), coupling constant (J Hz) and integration and assignment data for <sup>13</sup>C NMR spectra are reported as a chemical shift. High resolutions mass spectral analyses (HRMS) were carried out using ESI-TOF-MS.

### 2.4.2 Time-resolved Fluorescence Measurements

For time-correlated single-photon counting (TCSPC), we used a picosecond TCSPC machine from Horiba (Fluorocube-01-NL). The samples were excited at 375 nm using a picosecond diode laser (model: Pico Brite-375L), and the decays were collected at 440 nm. We used a filter on the emission side to eliminate the scattered light. The signals were collected at magic angle (54.75°) polarization using a photomultiplier tube (TBX-07C) as detector. The full width half-maximum (fwhm) of instrument response function of our setup is ~140 ps. The data analysis was performed using IBH DAS Version 6 decay analysis software. Throughout all the titration experiments we maintained temperature (T) at 25 °C. The decays were fitted with a multiexponential function.

 $D(t) = \sum_{i=1}^{n} a_i \exp(\frac{-t}{\tau_i})$ (S1)

Here D(t) denotes normalized fluorescence decay and  $a_i$  is the normalized amplitude of decay components  $\tau_i$ , respectively. The quality of the fit was judged by reduced chi square ( $\chi^2$ ) values and corresponding residual distribution. The acceptable fit has a  $\chi^2$  near unity.

#### 2.4.3 Materials

Glucose, oleic acid, TBHP and all other chemicals were purchased from Sigma-Aldrich or Merck, India and used without further purification. We used Millipore water (ultrapure level) throughout the experiments.

#### 2.4.4 Synthesis of -COOH functionalized CD (c-CD)

The carboxyl functionalized carbon dots (c-CDs) were synthesized by following a previously reported procedure with slight modification. In brief, 5 g of glucose in 10 ml of oleic acid was subjected to microwave irradiation using a focused microwave CEM discover reactor at 150 watts and 180 °C for 7 minutes. The resultant solid brownish product was dispersed in water and then was extracted by hexane several times in order to remove excess oleic acid. Finally the product was purified by dialyzing against ultra-pure water for 24 h to remove any excess precursors. 3.2 g of c-CDs were obtained as solid product after drying of solvents using a lyophilizer.

#### 2.4.5 Synthesis of reduced CD (r-CD)

The r-CDs were prepared by reducing the carboxyl functionalized c-CDs with NaBH<sub>4</sub>. Briefly, 0.5 g of NaBH<sub>4</sub> was added into an aqueous dispersion of c-CDs (5 mL solution with a c-CD concentration of 3mg/ml) and subjected to magnetic stirring at room temperature for 12 hrs. Finally the product was purified by dialyzing against ultrapure water for 24 h to remove excess NaBH<sub>4</sub> and lyophilized to obtain the solid r-CDs.

#### 2.4.6 Synthesis of -NH<sub>2</sub> functionalized CDs (n-CD)

The amine rich carbon dots (n-CDs) were synthesized by mixing urea and dextrose (2.5 g of dextrose and 2.5 g of urea) in 10 ml of oleic acid and subjected to microwave irradiation under similar conditions as that for c-CDs. The resultant solid product was dispersed in water and then was extracted with hexane for several times to remove excess oleic acid. The aqueous solution thus obtained

was subjected to dialysis against ultrapure water for 24 h to remove any excess precursors. The n-CDs were obtained as solid products (2.8 g) after removal of solvents using a lyophilizer.

### 2.4.7 Quantitative Measurement of -COOH and -OH functional groups in c-CDs

A quantitative estimation of hydroxyl and carboxyl functionality on the c-CD surface was evaluated using the Boehm titration as reported earlier.<sup>[36]</sup> A 5 mL aqueous solution containing c-CDs (1 mg/mL concentration) was first purged with argon for 1 h. Then the c-CD dispersion was titrated with aliquots of an aqueous sodium hydroxide solution (0.05 mol/L) to evaluate the total oxygenated functional groups. The mixture was titrated until a pH of 10.3 was achieved and the inflection point of the titration curve was measured by plotting the ratio of  $\Delta pH/\Delta V$  against the volume of NaOH. The concentration of functional groups calculated using the equation N<sub>1</sub>V<sub>1</sub>=N<sub>2</sub>V<sub>2</sub> was calculated to be 1.87 × 10<sup>-3</sup> mol/L.

The experiment was repeated for three times to obtain precise value.

For the measurement of carboxyl functional groups, a similar method was adopted except for titrating against sodium bicarbonate. A 5 mL aqueous dispersion of c-CDs (1 mg/mL concentration) was purged with Ar for 1 h and then titrated against an aqueous solution of sodium bicarbonate (0.05 mol/L). The pH was monitored using a pH meter and the titration was carried out until a pH of 8.10 was achieved. A graph was plotted for the ratio of  $\Delta pH/\Delta V$  against the volume of sodium bicarbonate and the total number of acid functional groups was calculated from the inflection point of the curve. The concentration of -COOH functional groups was found to be  $1.69 \times 10^{-4}$  mol/L using the equation N<sub>1</sub>V<sub>1</sub> = N<sub>2</sub>V<sub>2</sub>. The experiment was repeated thrice to ascertain precision. From the measurements, the ratio of -COOH: -OH on the c-CD surface was calculated to be 1:10. The surface functional group measurements were also carried out for the c-CDs recovered after the catalytic cycles.

### 2.4.8 Quantum Yield of C-dots

Quantum yield of C-dots at an excitation wavelength of 360 nm was calculated using the following equation

$$\Phi = \Phi_R \times I/I_R \times OD_R/OD \times \eta^2/\eta R^2$$
 S2

Where  $\Phi$  and I are the quantum yield and measured integrated emission intensity,  $\eta$  refractive index and OD the optical density. The subscript R refers to the reference fluorophore (Quinine sulphate,  $\Phi_R = 0.54$ ) of known quantum yield. The quinine sulphate was dissolved in 0.1 M H<sub>2</sub>SO<sub>4</sub> and C-dot was dissolved in Millipore water ( $\eta = 1.33$ ).

Table 2.4.8.1

Substance	Absorbance (360 nm)	Area	Refractive Index	Quantum Yield
Quinine sulphate	0.0762	854884.62	1.33	0.54
c-CD	0.0760	2135456.86	1.33	0.13
r-CD	0.0660	2308820.93	1.33	0.17
n-CD	0.0667	40739718.89	1.33	0.29

#### 2.4.9 Photocatalytic C-H bond oxidation of alkyl benzenes

In a typical reaction, 0.5 mmol of the substrate, 4 equivalents of TBHP and 15 mg of c-CD was taken in a sealed tube containing 3:1 v/v acetonitrile and H<sub>2</sub>O (Total amount of solvent was 4 ml). The photocatalytic reactions were performed using 60 watt white LED lamp (341 W cm<sup>-2</sup>) at room temperature under aerial conditions. Magnetic stirring was performed throughout the reaction. The progress of the reaction was monitored by TLC using ethyl acetate and hexane as eluent. After completion of the reaction, the resulting mixture was extracted with ethyl acetate (3 x 20 ml) and successively washed with water (1 x 15 ml). The organic solution was dried over anhydrous sodium sulphate and evaporation of the solvent on a rotary evaporator resulted in a residue. The residue was purified using silica gel column chromatography (100-200 mesh), where a mixture of hexane and ethyl acetate was used as eluent.

### 2.4.10 Monitoring the participation of c-CDs in the photocatalytic reaction

In order to confirm the participation of c-CDs in the photooxidation of C-H bonds, we performed a controlled experiment as follows:1.0 mmol of the tetralin, 4 equivalents of TBHP and 30 mg of c-CD was taken in a sealed tube

containing 8 ml of acetonitrile-water solvent mixture (3:1 v/v acetonitrile:H<sub>2</sub>O). The photocatalytic reaction was carried out using 60 watt white LED lamp at room temperature under magnetic stirring. The formation of the desired product tetralone was monitored from time to time by gas chromatography (GC). After 6 hours of reaction (approx. 50% of tetralone formation), the reaction was stopped and the reaction mixture was divided into 2 parts of 4 ml each. The photocatalytic reaction was carried out further with the 1<sup>st</sup> part of the reaction mixture to monitor the progress of the reaction. The 2<sup>nd</sup> part of the reaction mixture was subjected to ultracentrifugation (at 22000 rpm) upon which the c-CDs were precipitated out as a pellet. The resultant reaction mixture, without c-CDs was further exposed to visible light for photocatalytic reaction under similar reaction conditions as for part 1. Whereas in case of 1<sup>st</sup> part of the reaction mixture, the photocatalytic reaction progressed smoothly resulting in 90% of the desired product tetralone after 15 hours, no further product formation was observed in the 2<sup>nd</sup> part.

### 2.4.11 Recyclability studies of c-CDs

To study the recyclability of performance of c-CDs, the model photocatalytic conversion of tetralin to tetralone was performed in cycles of reactions under standard photocatalytic reaction conditions. After the completion of the 1<sup>st</sup> cycle of the reaction, the organic products were extracted using ethyl acetate, while the c-CDs remained in the reaction medium. The 2<sup>nd</sup> cycle of the photocatalytic reaction was carried out using the c-CDs containing reaction mixture, where tetralin and TBHP was added without addition of any external CDs. Thus the same c-CDs could be reused at least for three runs. The c-CDs showed efficient recyclability as a photocatalyst and 81% of the desired oxidized product could be obtained after the third cycle.

### 2.4.12 Radial Scavenging Analysis

To explore the involvement of various free radicals during the photocatalytic reaction, different known radical scavengers were added in the reaction medium and the model photocatalytic reaction for the conversion of tetralin to tetralone was studied in presence of visible-light under standard reaction conditions. Whereas butylated hydroxytoluene (BHT) was used as a scaverger for studying the involvement of radicals in the mechanism, benzoquinone (BQ) was used as a superoxide radical scavenger, *tert*-butyl alcohol (TBA) as 'OH radical scavenger, EDTA as hole  $(h^+)$  scavenger and AgNO<sub>3</sub> as electron scavenger.

#### 2.4.13 Isolation of hydroperoxy intermediate: 0.5 mmol 2-methoxyxanthene

0.5 mmol of 2-methoxyxanthene, 4 equivalents of TBHP and 15 mg of c-CD was taken in a sealed tube containing 4 mL solvent (3:1 v/v acetonitrile and H<sub>2</sub>O) and the photochemical reaction was carried out using a 60 watt white LED lamp (341 W cm<sup>-2</sup>) at room temperature under aerial conditions. The reaction was stopped after 4 h and was extracted with ethyl acetate. The organic solution was dried over anhydrous sodium sulphate and the solvent was evaporated on a rotary evaporator. The residue was purified using silica gel column chromatography (100-200 mesh) using 2 % hexane and ethyl acetate solvent system.

#### 2.4.14 Photocurrent response measurements

Commercial indium tin oxide (ITO) was used as the substrate for electrode build-up, and cleaned by sonication sequentially for 20 min each in acetone, 10% KOH in ethanol and doubly deionized water. Photoelectrochemical experiments were performed in a conventional three-electrode cell (Pyrex window) with a platinum wire as the auxiliary electrode and an Hg/HgCl<sub>2</sub> (saturated KCl) as the reference electrode. The working electrodes were ITO/c-CDs, with the glass side facing the incident light. They were prepared by spreading aqueous slurries over ITO glass substrates. Lithium perchlorate (LiClO<sub>4</sub>) in acetonitrile was used as a electrolyte in cells. A 60 W white LED light was used as light source and positioned 4 cm away from the photoelectrochemical cell. The photocurrent signal was recorded with a CHI 660C workstation (CH Instruments, Chenhua, Shanghai, China) connected to a personal computer. All electrochemical experiments were carried out at room temperature.

### 2.4.15 Characterization data

### 2.4.15.1 Characterization data for hydroperoxy intermediate

**9-Hydroperoxy-4-methoxy-9H-xanthene:** Yellowish oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.6 (d, J = 8.7, 1H), 7.41-7.37 (t, J = 8.28, 1H), 7.34-7.32 (d, J = 7.28, 1H), 7.19-7.17 (t, J = 7.52 Hz, 1H), 7.16-7.14 (d, J = 8.28 Hz, 1H), 7.09-7.07 (t, J = 7.8 Hz, 1H), 6.98-6.96 (d, J = 8 Hz, 1H), 5.95 (s,1H), 3.95 (s,3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 152.5, 147.9, 142.5, 131.3, 129.9, 122.9, 122.9, 122.4, 119.8, 119.0, 116.9, 112.0, 80.3, 56.3; Mass: 244.07, HRMS (ESI): calcd for [C<sub>14</sub>H<sub>12</sub>O<sub>4</sub><sup>+</sup> + Na+] 267.0612, found 267.0623.

### 2.4.15.2 Characterization data of synthesized oxidized products

3,4-Dihydro-2*H*-naphthalen-1-one (1a): Light yellow oil; <sup>1</sup>H NMR (400 MHz,

CDCl<sub>3</sub>)  $\delta$  8.03 (dd, J = 7.9, 1.2 Hz, 1H), 7.46 (dt, J = 7.53, 1.49 Hz, 1H), 7.31-7.23 (m, 2H), 2.96 (t, J = 6 Hz, 2H), 2.65 (t, J = 6 Hz, 2H), 2.13 (quintet, J = 6 Hz, 2H) ; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  198.4, 144.5, 133.4, 132.6, 128.7, 127.1, 126.6, 39.2, 29.7, 23.3; HRMS (ESI): calcd for [C<sub>10</sub>H<sub>10</sub>O<sup>+</sup>+Na<sup>+</sup>] 169.0624, found 169.0629.

Indan-1-one (2a): Light Yellow Oil; <sup>1</sup>H NMR (400 MHz, CDCl3)  $\delta$  7.74(d, J = 7.9 Hz, 1H), 7.56 (t, J = 2.1 Hz, 1H), 7.45 (d, J = 8.1 Hz, 1H), 7.36 (t, J = 7.7 Hz, 1H), 3.14 (t, J = 5.9 Hz, 2H), 2.69 (t, J = 6.2 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl3)  $\delta$  207, 155, 137, 134, 127, 124, 36, 30, 25; HRMS (ESI): calcd for [C<sub>9</sub>H<sub>8</sub>O<sup>+</sup>+ Na<sup>+</sup>] 155.0467, found 155.0472.

**Benzophenone (3a):** White solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.82(m, 4H), 7.59(m,2H),7.49(m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  196.7, 137.6, 132.4, 130.0, 128.2; HRMS (ESI): calcd for [C<sub>13</sub>H<sub>10</sub>O<sup>+</sup>+Na<sup>+</sup>] 205.0624, found 205.0632.

**4-(Methoxyphenyl)(phenyl)methanone (4a):** White solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.83-7.81(d, 2H *J*=8.3), 7.75-7.74 (d,2H *J*=4.4),7.48-7.44(d, 2H, *J*=7.52), 6.97-6.95(d, 2H, *J*=7.76), 3.83 (s, 3H) ; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  195.3, 162.9, 138, 132.2, 131.6, 121.8, 129.4, 127.9, 113.2, 55.2; HRMS (ESI): calcd for [C<sub>14</sub>H<sub>12</sub>O<sub>2</sub><sup>+</sup>+ Na<sup>+</sup>] 235.0730, found 235.0738.

**9***H***- flouren-9-one (5a):** White solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.66 (d, *J* = 6.9 Hz, 1H), 7.52-745 (m, 4H), 7.30 (dt, *J* = 7.1, 1.3 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  193.9, 144.4, 134.7, 129.1, 124.3, 120.3; HRMS (ESI): calcd for [C<sub>13</sub>H<sub>8</sub>O<sup>+</sup>+ Na<sup>+</sup>] 203.0467, found 203.0477.

Acenaphthylen-1(2H)-one (6a): Yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ 8.1 (d, *J* = 8.3, 1H), 7.97 (d, *J* = 8.6, 7.04, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.73 (t, *J* = 8.6 Hz, 1H) 7.61(t, *J*=8.04,1H) 7.47(d, *J*=7.04,1H) 3.82(s,2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  203, 134.7, 131.5, 130.9, 128.4, 128, 123.9, 121.4, 121, 119, 118; HRMS (ESI): calcd for [C<sub>12</sub>H<sub>8</sub>O<sup>+</sup>+ Na<sup>+</sup>] 191.0467, found 191.0476.

**1-(naphthalene-2-yl)ethanone (7a):** Yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.46 (s, 1H), 8.04 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.95-7.90 (m, 2H), 7.68-7.60 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  198.1, 135.6, 134.5, 132.5, 130.2, 129.5, 128.5, 128.4, 126.8, 123.9, 26.7; HRMS (ESI): calcd for [C<sub>12</sub>H<sub>10</sub>O<sup>+</sup>+ Na<sup>+</sup>] 193.0624, found 193.0632.

Anthracene-9, 10-dione(8a): Yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.4 (dd, J = 5.9, 3.4Hz, 4H), 7.6 (dd, J = 5.9, 3.5 Hz, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  183.1, 134.1, 133.5, 132.7, 128.4, 127.6, 127.2; HRMS (ESI): calcd for [C<sub>14</sub>H<sub>8</sub>O<sub>2</sub><sup>+</sup>+ Na<sup>+</sup>] 231.0417, found 231.0429.

Anthracene(8a<sup>'</sup>): White solid<sup>; 1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.43(s, 2H), 8.01 (dd, J = 6.3, 3.6Hz, 4H), 7.48 (dd, J = 6.6, 3.6 Hz, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  131, 128, 126, 125; HRMS (ESI): calcd for [C<sub>14</sub>H<sub>10</sub><sup>+</sup>+ Na<sup>+</sup>] 201.0675, found 201.0689.

**9***H***-xanthen-9-one (9a):** White solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.34 (dd, *J* = 8.1, 1.6 Hz,2H), 7.71 (dt, *J* = 8.6, 1.8 Hz, 2H), 7.5 (d, *J* = 8.5 Hz, 2H), 7.39 (t, *J* = 7.9 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  177, 156, 135, 127, 124, 122, 118; HRMS (ESI): calcd for [C<sub>13</sub>H<sub>8</sub>O<sub>2</sub><sup>+</sup>+ Na<sup>+</sup>] 219.0417, found 219.0431.

**4-Methoxy-9H-xanthen-9-one (10a):** White solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.34 (dd, J = 8.04, 1H), 7.91 (d, J = 8.6, 1.8 Hz, 1H), 7.5 (d, J = 8.5 Hz, 2H), 7.39 (t, J = 7.9 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  177.2, 156, 148.6, 134.8, 126.7, 124.1,123.4,122.7,121.7, 118.3,117.7,115.4,114,56.4; HRMS (ESI): calcd for [C<sub>14</sub>H<sub>10</sub>O<sub>3</sub><sup>+</sup>+ Na<sup>+</sup>] 249.0522, found 249.0531.
**2-Hydroxy-9H-xanthen-9-one (11a):** White solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.23 (d, J = 8.5, 1H), 8.12 (d, J = 8.8, 1H), 7.9 (t, J = 7.04 Hz, 1H), 7.68 (d, J = 8.52 Hz, 1H), 7.52 (t, J = 7.28, 1H), 6.98(t, J = 8.52, 1H), 6.74 (d, J = 8.28, 1H), 5.8 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  176.3, 156.2, 154.3,149.2, 134.6, 126.1, 124.3,123.9,121.5,120.1, 118.1,117.6,107.6; HRMS (ESI): calcd for [C<sub>13</sub>H<sub>8</sub>O<sub>3</sub><sup>+</sup>+ Na<sup>+</sup>] 235.0366, found 235.0379.

**4-Chloro-9H-xanthen-9-one (12a):** White solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.32 (d, J = 8.1, J = 8.2,1H), 8.04 (d, J = 8.5, 1H), 7.7 (t, J = 7.76 Hz, 1H), 7.69 (d, J = 7.9 Hz, 1H), 7.53 (s, J = 7.5 Hz, 1H), 7.49 (t, J = 7.9 Hz 1H), 7.35 (d, J = 7.56 Hz, 1H);<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 177.3, 155.6, 153.8,149.6, 135.3, 125.5, 124.1,123.7,121.2,120.4, 118,117.7,108.6; HRMS (ESI): calcd for [C<sub>13</sub>H<sub>7</sub>ClO<sub>2</sub><sup>+</sup>+ Na<sup>+</sup>] 253.0027, found 253.0043.

**Isochroman-1-ol (13a):** White oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.27 (d, *J* = 7.2, 1H), 7.21-7.12 (m, 2H), 7.06 (d, *J* = 7.5 Hz, 1H), 5.96 (s, 1H) 4.17-4.1(m, 1H) 3.94-390, (m, 1H) 2.99-2.90(m,1H),2.54-2.49 (dd, *J*=3Hz, 2.5Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  136, 130, 129, 128, 126, 99, 58, 28; HRMS (ESI): calcd for [C<sub>9</sub>H<sub>10</sub>O<sub>2</sub><sup>+</sup>+ Na<sup>+</sup>] 173.0573, found 173.0586.

**Nicotinaldehyde (15a):** Colourless liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.1 (s, 1H), 8.8 (s,1H), 7.99-7.9 (m, 2H), 7.59-7.53 (t, 1H, *J*=7.52); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  193.6, 153.0, 150.4, 137.3, 128.1,121.9; HRMS (ESI): calcd for [C<sub>6</sub>H<sub>5</sub>NO<sup>+</sup>+ Na<sup>+</sup>] 130.0263, found 130.0276.

**1-(pyridin-3-yl)ethanone (16a):** Colourless liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.7-8.69 (s,1H), 8.05-7.86 (d,1H J=7.76), 7.84-7.82 (t, *1*H, J=), 7.5-7.46 (m, 1H), 2.73(s,3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  200, 153.6, 149, 136.8, 127.1, 121.6, 25.7; HRMS (ESI): calcd for [C<sub>7</sub>H<sub>7</sub>NO<sup>+</sup>+ Na<sup>+</sup>] 144.0420, found 144.0437.

**Isoquinoline (17a):** Brownish liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.2 (s,1H), 8.52 (d ,1H J=5.76), 7.98 (d, 1H, J=7.76), 7.83 (d, 1H, J=8.04), 7.7-7.5 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  152.2, 142.7, 135.5, 130.1, 128.5, 127.3, 127.0, 126.2, 120.2; HRMS (ESI): calcd for [C<sub>9</sub>H<sub>7</sub>N<sup>+</sup>+ Na<sup>+</sup>] 152.0471, found 152.0487.

**Benzaldehyde (1b):** Colourless liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.02 (s, 1H), 8.13 (d, J = 7.3 Hz. 2H), 7.89 (d, J = 7.2 Hz, 2H), 7.61 (t, J = 7.8 Hz, 1H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 192.4, 136.3, 134.4, 130.1, 129.7, 128.9, 128.4; HRMS (ESI): calcd for [C<sub>7</sub>H<sub>6</sub>O<sup>+</sup>+ Na<sup>+</sup>] 129.0311, found 129.0327.

**4-chlorobenzaldehyde (3b):** Colourless liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.98 (s, 1H), 7.83 (d, *J*= 8.3 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  191, 141, 134, 131, 129; HRMS (ESI): calcd for [C<sub>7</sub>H<sub>5</sub>ClO<sup>+</sup>+ Na<sup>+</sup>] 162.9921, found 162.9931.

**4-bromobenzaldehyde (5b):** Colourless liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.97 (s, 1H), 7.5 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  191.6, 145.1, 133.8, 129.8, 129.4, 129.3, 21.5; HRMS (ESI): calcd for [C<sub>7</sub>H<sub>5</sub>BrO<sup>+</sup>+ Na<sup>+</sup>] 206.9416, found 206.9433.

**4-methylbenzaldehyde (6b):** White solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.95 (s, 1H), 7.78 (d, *J*= 8 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 2.43 (s, *3*H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  191.6, 145.7, 133.8, 129.4, 129.3, 21.5; HRMS (ESI): calcd for [C<sub>8</sub>H<sub>8</sub>O<sup>+</sup>+ Na<sup>+</sup>] 143.0467, found 143.0475.

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Appendix-Chapter 2

<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Hydroperoxy Intermediate and oxidized product



<sup>1</sup>H NMR spectra for hydroperoxy intermediate



<sup>13</sup>C NMR spectra for hydroperoxy intermediate.





































Visible-Light Induced Enhancement in Multi-catalytic Activity of Sulfated Carbon dots for Aerobic Carbon-Carbon Bond Formation

#### **3.1 Introduction**

The use of carbonaceous materials as catalysts for various organic transformations has become increasingly attractive as metal-free alternatives to inorganic catalysts. The interest in using 2-dimensional graphene oxide and its derivatives as carbocatalysts is growing as they demonstrate both oxidative and acidic catalytic activity making it possible to integrate multiple "tandem" or "relay" catalysis in one pot.<sup>[1-6]</sup> On the other hand, the zero-dimensional carbon dots, with interesting emission properties tunable through modification in surface functionalities or doping with heteroatoms, can offer an added advantage, as they demonstrate efficient visible-light photocatalytic activity.<sup>[7-9]</sup> The tunable photoluminescence, arising from both quantum-confinement effects and surface functional groups along with upconversion emission properties, offers exciting applications.<sup>[10-11]</sup> Visible-light opportunities for photocatalytic driven photocatalytic processes have emerged as an important tool for various organic transformations, where transfer of energy and electrons from a light absorbing photocatalyst to non-absorbing molecules provide a green and sustainable pathway under mild reaction conditions.<sup>[12-14]</sup> Usually another catalyst (inorganic Lewis acid or organocatalyst) is combined with the photoredox system to act on different substrates in the same reaction pot. For example, photochemical organic transformations using tandem photoredox-Lewis acid catalyst has been reported recently.<sup>[15-16]</sup> Although ruthenium and iridium photoredox catalysts demonstrate high efficiency, the rarity and the cost of the resources are matter of concern. Furthermore, the possibility of poisoning of one catalyst by another is often associated with such multicatalytic combinations.<sup>[17]</sup> In this regard, carbon dots, which are easily synthesized from commonly available biomolecules and biomasses, can be developed as a cheap, biocompatible and metal free catalyst having both photooxidative and acidic properties in a single entity through judicious surface engineering.

Cross-dehydrogenative coupling (CDC) has been developed as an important methodology in synthetic chemistry to activate C-H bonds resulting in the formation of carbon-carbon and carbon-heteroatom bonds in complex natural products and pharmaceuticals.<sup>[18-20]</sup> Under oxidative conditions, two C-H bonds from two different molecules can be coupled to form a new C-C bond with

hydrogen as the only leaving group and water as the sole byproduct in most cases. Usually transition metal catalysts are used as catalysts for the CDC reactions in the presence of external oxidants.<sup>[21-24]</sup>A metal-free CDC pathway was reported by Klussmann et. al. where aerobic oxidative coupling of activated benzylic electrophiles with several nucleophiles such as aldehydes, ketones and 1,3-dicarbonyl compounds, could be realized using organic acids as catalysts.<sup>[25-</sup> <sup>27]</sup> Although a wide range of substrates could be coupled, the yield of the coupling products was poor and required longer reaction time. The use of carbocatalysts for C-C cross-coupling was very recently reported by Loh et al. where graphene oxide was coupled with triflic acid for aerobic cross-coupling of xanthenes and 1,2-dimethoxybenzene.<sup>[28]</sup> However, in absence of triflic acid, only the oxidized product of xanthene was obtained. The use of strong mineral and organic acids such as sulphuric acid, methanesulphonic acid, triflic acid and p-toluensulphonic acid as catalysts are often associated with serious disadvantages like corrosion, toxicity and separation from reaction mixture as well as waste stream neutralization.<sup>[29-30]</sup> Therefore, the development of a mild and non-toxic carbocatalytic system for the C-C cross-coupling reactions is much desired for maintaining overall sustainability.

We envisioned that a combination of photooxidation and surface acidity might be influential in high yield of the coupling products in a shorter reaction time. We earlier exploited the inherent photocatalytic and surface acidic properties of carbon dots for benzylic C-H oxidation and carbon-heteroatom bond formation.<sup>[31]</sup> In this chapter, we report that sulfonated carbon dots can be used as cost-effective and metal-free catalysts for the CDC coupling of benzylic hydrocarbons with a variety of nucleophilic coupling partners such as ketones, diketones, and arenes under mild reaction conditions by taking advantage of their visible-light induced photocatalytic and surface acidic properties.

#### **3.2 Results and discussion**

#### 3.2.1 Synthesis and characterization of Carbon dots

Acidic carbon dots surface functionalized with -COOH (c-CDs) and -SO<sub>3</sub>H groups (s-CDs) were synthesized by carbonization of glucose and further treatment of the c-CDs with fuming sulfuric acid respectively.<sup>[32]</sup> Transmission

electron microscopy studies of s-CDs showed the formation of quasi spherical and fairly mono disperse particles. The particles had a size distribution in the range of 2-6 nm (average diameter of  $3.2 \pm 1.5$  nm) as calculated from measurement of over hundred particles (Figure 3.1a and c). The high resolution TEM image of s-CDs showed the appearance of lattice fringes signifying the (102) lattice of graphitic carbon (Figure 3.1b). Selected area electron diffraction (SAED) pattern confirmed the crystallinity of the synthesized CDs (Figure 3.1c inset). The powder X-ray diffraction spectra of s-CDs showed a broad peak centred at  $2\theta = 23.1^{\circ}$ , corresponding to a d-spacing of 3.9 Å, which supports the introduction of functional groups on the graphitic plane as the interfacing distance is greater than that of graphite (3.4 Å) (Figure 3.1d). The s-CD aqueous solution showed excitation-dependent emission properties with the maximum emission at 424 nm upon excitation at 300 nm and the photoluminescence shifted to longer wavelength with increasing excitation wavelength (Figure 3.1e). The Raman spectrum shows both the G band at 1586 cm<sup>-1</sup> owing to in-plane vibrations of the  $sp^2$  carbons and the D band at 1346 cm<sup>-1</sup> signifying the presence of sp<sup>3</sup> defects (Figure 3.1f). The UV-visible spectrum of the aqueous solution showed a peak at 268 nm owing to the  $\pi$ - $\pi$ \* transition of nanocarbon (Figure 3.2) a). The presence of functional groups was supported by the FTIR studies, which showed a broad peak at  $3436 \text{ cm}^{-1}$ , that can be assigned to the O-H functionality and prominent peaks at 2927 cm<sup>-1</sup> (C-H), 1703 cm<sup>-1</sup> (C=O), 1627 cm<sup>-1</sup> (C=C). The characteristic peak at 1038  $\text{cm}^{-1}$  and 1002  $\text{cm}^{-1}$  attributed to the O=S=O stretching vibrations in -SO<sub>3</sub>H groups and peak at 1166 cm<sup>-1</sup> for SO<sub>3</sub>H stretching which indicate the successive incorporation of sulfonic acid groups on carbon dots surface (Figure 3.2b and c). A quantitative assessment of the surface functional groups was carried out by standard titration methods, which suggest the presence of -OH (1.3 × 10<sup>-3</sup> mol/L), -COOH (0.5 × 10<sup>-3</sup> mol/L) and -SO<sub>3</sub>H (0.4 × 10<sup>-3</sup> mol/L) functionalities on the s-CD surface.

#### 3.2.2 Optimization studies and substrate scope

The initial assessment for the catalytic activity of carbon dots bearing acidic functionalities was conducted for the aerobic cross-coupling of xanthene and cyclohexanone. On performing the reaction using c-CDs as a catalyst under solvent-free and  $O_2$  rich environment (1 bar) at 70 °C for 10 h (entry 2, Table

3.1), the coupling product (3ab) was obtained in 22% yield with xanthenone (3a) as the major byproduct. On the other hand, under similar reaction conditions, s-CDs afforded 31% of the coupling product (entry 3, Table 3.1). Under open air condition, the auto-oxidative coupling was rather sluggish and only15% of the coupling product was obtained at 70 °C after 10 h (entry 4, Table 3.1). A dramatic enhancement in the formation of the coupling product (91% isolated yield) in a



**Figure 3.1.** (a) TEM image of s-CDs; (b) high resolution TEM image showing the lattice fringes; (c) histogram for size distribution of s-CDs, inset SAED pattern; (d) powder XRD spectra s-CDs showing a broad peak at  $2\theta = 23.1^{\circ}$ ; (e) emission spectra of s-CDs, while excited at variable wavelengths; and (f) Raman spectra of s-CDs, showing the D and G band of graphitic carbon.



Figure 3.2. (a) UV-visible spectra of s-CDs in water; the band at 278 nm signifies  $\pi$ - $\pi$ \* transition, (b) Full scan FTIR spectrum recorded using KBr which shows the presence of – OH, C=O, C=C, -SO<sub>3</sub>H functionalities on s-CD surface, (c) Magnified FTIR spectrum of s-CDs, shows peaks at 1703 cm<sup>-1</sup> (C=O), 1627 cm<sup>-1</sup> (C=C), Peaks at 1038 cm<sup>-1</sup> and 1002 cm<sup>-1</sup> are attributed to the O=S=O stretching vibrations in -SO<sub>3</sub>H groups and peak at 1166 cm<sup>-1</sup> for -SO<sub>3</sub>H stretching.

Entry	Catalyst	Solvent	Time	Yield <sup>b</sup>	Sel
			(h)	(%)	(%)
1		Ethyl acetate	12	Trace	-
2	$c-CD(\Delta)$		10	22	66
3 <sup><i>c</i></sup>	s-CD ( $\Delta$ )		5	31	83
$4^d$	s-CD (hv)/( $\Delta$ ) (air)		5/10	23/15	93
5	s-CD (hv)		3	91	<b>98</b>
6 <sup><i>e</i></sup>	s-CD (hv) (argon)		5	4	96
$7^{f}$	s-CD (hv) +TBHP		3	17	92
$8^g$	s-CD ( $h\nu$ )+H <sub>2</sub> O <sub>2</sub>		3	26	93
9	s-CD (hv)	Ethyl acetate	12	46	95
10	s-CD (hv)	DCM	12	10	96
11	s-CD (hv)	ACN	12	18	93
12	s-CD (hv)	MeOH	12	15	95
13 <sup><i>h</i></sup>	s-CD (hv)+ Catalase		3	86	94

<sup>*a*</sup>Unless otherwise specified, all the reactions were carried out with xanthene (0.5 mmol) and cyclohexanone (3 mmol) as the model substrates; s-CD as catalyst (5 mg) illuminated under a 34 W blue LED lamp (hv = 425 nm) at 25 °C under O<sub>2</sub> environment, <sup>*b*</sup>Isolated yield, <sup>*c*</sup>Reactions under dark condition at 70 °C, <sup>*d*</sup> under air, <sup>*e*</sup>under Ar environment, <sup>*f*</sup>TBHP, <sup>*g*</sup>H<sub>2</sub>O<sub>2</sub>, <sup>*h*</sup>Catalase.

shorter reaction time (3 h) was observed when the reaction was performed under visible-light illumination at room temperature (entry 5, Table 3.1). In comparison, c-CDs or pyrene-1-carboxylic acid (PCA) could afford only 20% and 15% respectively of the coupling product under visible-light irradiation and significant amount of xanthenone was formed as byproduct in both cases (entry 5-6, Table 3.2). For comparison, we also studied the carbocatalytic activity of graphene oxide and sulfonated graphene oxide (s-GO), which afforded the coupling product with a much lower yield (39% and 48% respectively), at 70 °C for 10 h (entry 9-11 Table 3.2). Using commonly available acids such as H<sub>2</sub>SO<sub>4</sub>, benzoic acid and *p*-toluene sulfonic acid also could afford the coupling product with significant yield, although they required a much longer reaction time (entry 2-4, Table 3.2). The oxidized product of xanthene, 3a, was obtained as the major product when the reaction carried out in absence of any catalyst. Performing the photocatalytic reaction using s-CD as the carbocatalyst under argon atmosphere resulted in insignificant yield of the product (4%), which proves that O<sub>2</sub> is the

terminal oxidant and the s-CDs can serve as an oxidant only to a small extent (entry 6, Table 3.1). The use of external oxidants such as  $H_2O_2$  or tert-butyl hydroperoxide (TBHP) resulted in lower yields (entry 7-8, Table 3.1). Solvent screening studies using a variety of solvents suggested that the best results are obtained under solventless conditions (figure 3.2).



**Figure 3.3.** Cross-coupling of xanthene (0.5 mmol) and cyclohexanone (3 mmol) using various acid catalysts and carbocatalysts, using a 34 W blue LED lamp (hv = 425 nm) at 25 °C under  $O_2$  environment. The reactions (1 to 7) were performed for 12 h, whereas the reactions (8 to 10) were carried out for 3 h, 7 mol% of acid catalysts were used in the reactions (3, 4, 5, 6 and 9).

Using the optimized conditions, the effectiveness of s-CDs as photocatalyst was evaluated for coupling a range of benzylic hydrocarbons and nucleophiles. Cyclic  $\alpha$ -ketones such as cyclopentanone, cyclohexanone, cycloheptanone could be coupled with xanthene to give their corresponding 1-(9'xanthyl)-substituted ketones with good isolated yield (80%-93%, Entries 3aa-3ae Table 3.3) within 3-5 h under visible light irradiation. Cyclic  $\alpha$ -ketones could also be amicably coupled with thioxanthene leading to the formation of C-C coupling products with high yield (Entries 3ba-3bb, Table 3.3). A cyclic ketone such as 2pentanone can also be coupled efficiently with xanthene and thioxanthene to afford the corresponding coupling products in high yield within a short reaction time (Entry 3ca, Table 3.3). Other nucleophiles such as  $\beta$ -keto esters and 1,3-

Entry	Catalyst	Time (h)	3ab <sup>b</sup> Yield (%)	$3a^b$ Yield (%)
1	$^{c}CH_{3}COOH (hv)/(\Delta)$	12	12/7	Trace
2	$^{c}\text{H}_{2}\text{SO}_{4}(\text{conc}) (hv)/(\Delta)$	12	68/62	Trace
3	<sup>c</sup> Benzoic acid $(hv)/(\Delta)$	12	16/14	Trace
4	<sup>c</sup> PTSA (hv)/( $\Delta$ )	12	64/69	Trace
5	$^{d}$ CD (hv)	3	20	26
6	<sup>c</sup> PCA (hv)	3	15	23
7	$^{d}$ s-CD (hv)	3	91	Trace
8	$^{d}$ s-CD ( $\Delta$ )	10	36	20
9	$^{d}$ GO ( $\Delta$ )	10	39	32
10	$^{d}$ s- GO (hv)/( $\Delta$ )	10	38/42	22/24
11	$e^{s}$ - GO (hv)/( $\Delta$ )	10	43/48	29/26

Table 3.2. Performance of various catalysts for the model coupling reaction<sup>a</sup>

<sup>a</sup>Unless otherwise specified, all the reactions were carried out with 2-methoxy xanthene (0.5 mmol) and Cyclohexanone (3 mmol) as the model substrates; using 34 W blue LED lamp (hv = 425 nm) at 25 °C under  $O_2$  environment;  $\Delta =$  Reaction performed without visible-light illumination at 70 °C; <sup>b</sup>Isolated yield; <sup>c</sup>catalyst (7 mol%), <sup>d</sup>catalyst (5.0 mg); <sup>e</sup>catalyst (30 mg).

diesters also could be coupled with xanthene and thioxanthene under the optimal conditions. When ethyl acetoacetate, dimethylmalonate reaction or diethylmalonate were coupled with xanthene and thioxanthene, their corresponding C-C coupling products were obtained with high isolated yield (74%-96%, Entries 3ea-3fc Table 3.3). In addition, we expanded the substrate scope of the C-C coupling reaction to other heteroaromatic benzylic hydrocarbon with various nucleophiles under visible light irradiation. Isochroman and Nphenyltetrahydroisoquinoline could be coupled effectively with cyclic  $\alpha$ -ketones and acetophenone derivatives to obtain the coupling products with significant yield (Entries 3ga-3jc, Table 3.3). In several of the coupling products, the formation of diastereomers was clearly observed from the <sup>1</sup>H NMR studies, in most cases with high diastereomeric ratio (Table 3.4). Further, we investigated the activity of other benzyl compounds, such as diphenylmethane, Indan and tetralin, to form coupling products with cyclohexanone, however all these substrates were found to be inactive under the present reaction conditions. Next, the compatibility of the methodology for the CH-CH coupling reaction was reaction was evaluated through the reaction of xanthene derivatives with various arenes under visible light irradiation (Scheme 3.1). s-CDs show excellent

Product		Time (h)	Yield $(\%)^b$	Entry
		3	93	3aa
o / n	n=1, $R=H R'=H$	3	91	3ab
R	n=2 $R=H$ $R'=H$	5	86	3ac
	$n=2 R=H R'=-OCH_3$	3	77	3ad
R' 3a	n=2 R=OH R <sup>/</sup> =H	5	89	3ae
	n=3 $R=H$ $R'=H$			
	,			
0 / n	n=2 $R=H$ $R'=H$	5	87	3ba
S	n=3 R=H R $'$ =H	8	83	3bb
3b				
O II	$R = -CH_3 R' = -C_2H_5$	12	76	3ca
R R'	$R = -C_6H_5 R' = H$	5	82	3cb
	$R = -C_6H_5 R' = -CH_3$	10	88	3cc
~ 0 ~				
50				
0 ∦ ₽′				
R	R=4 Me-C <sub>6</sub> H <sub>5</sub> R <sup><math>/</math></sup> = -CH <sub>3</sub>	10	86	3cd
		9	85	3da
S	$\mathbf{R} = -\mathbf{C}_6\mathbf{H}_5 \ \mathbf{R}' = \mathbf{H}$			
3d				
o o				
R R'	R. $R' = -OCH_3$	12	93	3ea
	R, $R^{/}$ = -OC <sub>2</sub> H <sub>5</sub>	12	96	3eb
	$R = -CH_3 R' = -OCH_3$	12	74	3ec
3e				
0 0				
	R, R <sup><math>\prime</math></sup> =-OCH <sub>3</sub>	12	89	3fa
	$R, R' = -OC_2H_5$	12	91	3fb
s	$R = -CH_3 R' = -OCH_3$	15	68	3fc
3f				

 Table 3.3. Photocatalytic C-C coupling reaction of Benzylic Hydrocarbons and various nucleoplies

Chapter 3				
	n=1	5	83	3ga
0 () n	n=2	5	81	3gb
C O	n=3	5	78	3gc
3g				
0 	$R = -C_6H_5 R' = H$	5	73	3ha
R	$R = -C_6H_5 R' = -CH_3$	5	86	3hb
O O	$R = 4 Me - C_6 H_5 R' = -$	5	78	3hc
3h	CH <sub>3</sub>			
	n=1	5	76	3ia
N <sup>Pn</sup>	n=2	5	80	3ib
3i	n=3	10	74	3ic
O P/				
R	$R = -C_6H_5 R' = H$	8	87	3ja
N <sup>-Pn</sup>	$R = -C_6H_5 R' = -CH_3$	8	81	3jb
	$R = 4 Me - C_6 H_5 R' = -$	8	82	3jc
3j	CH <sub>3</sub>			-

<sup>*a*</sup>Unless specified, all the reactions were carried out with the substrate (0.5 mmol) and ketone (3.0 mmol) using s-CD as catalyst (5.0 mg) under solventless conditions using a 34 W blue LED lamp (hv = 425 nm) at 25 °C under O<sub>2</sub> environment; <sup>*b*</sup>Isolated yield.

Table 3.4. Diasteriomeric coupling product yield

Product	Diasteriometric Ratio
3hc	2.9:1
3ia	0.92:1
3ib	1.3:1
3ic	1:1
3jb	1:1
6b	1:0.92

photocatalytic activity for the CH-CH coupling of xanthene and its derivatives and an electron-rich arene, *meta*-dimethoxybenzene to afford the corresponding coupling products in 80-92% isolated yields, although the reaction required relatively longer duration (12 h).

**Scheme 3.1.** Photocatalytic CH-CH coupling reaction of benzylic hydrocarbons and various arenes<sup>a</sup>



<sup>a</sup>All the reactions were carried out with substrate (0.5 mmol) and arene (3 mmol) using s-CD as catalyst (5 mg); using 34 W blue LED lamp (hv = 425 nm) at 25 °C for 12 h under an  $O_2$  environment.

#### 3.2.3 Recovery and Recyclability

To further ensure whether the catalysis process is surface catalyzed or due to any leached active species, we performed the model coupling reaction under optimal reaction conditions. The reaction was stopped after 50% conversion and the s-CD catalyst was removed from the reaction mixture by centrifugation. The reaction was further continued with the supernatant for 10 h under visible light irradiation; however no further coupling product was formed (Figure 3.3a). The results clearly suggest that the catalytic process is truly heterogeneous in nature. The s-CDs could be readily recovered and recycled for at least four runs without any significant impact on the yield of the product (76%, isolated yield) (Figure 3.3 b).

The recovered s-CDs after the fourth cycle were analyzed to determine the relationship between the catalytic reactivity and surface functionalities. The TEM study revealed that there is no pronounced morphological change (Figure 3.5a). From the emission spectra of the recovered s-CDs, a minor blue shift in the emission peak as well as an enhancement in the fluorescence intensity was


**Figure 3.4.** a) Reaction profile for the model coupling reaction under visible light irradiation (red) and after the s-CDs were removed by centrifugation from the reaction mixture (blue), b) Recyclability test for monitoring the efficiency of s-CDs as a photocatalyst for the coupling reaction in a cycle of reactions.

observed as compared to the pristine ones (Figure 3.5b). This suggests a possible partial reduction of the surface in the -SO<sub>3</sub>H functionality in the recovered s-CDs.<sup>[33]</sup> This was further evidenced from FTIR studies, where the band at 1038  $cm^{-1}$  associated with O=S=O and the band at 1166  $cm^{-1}$  corresponding to -SO<sub>3</sub>H groups are reduced significantly (Figure 3.5c). The elemental analysis also supports the obtained result (Table 3.5). The S2p core level XPS spectra showed that the amount of SO<sub>3</sub>H functionality (169.7 V) is reduced in the recovered s-CDs as compared to the pristine ones (Figure 3.6). A comparative C1s core level XPS spectra of the pristine and recovered s-CDs show no significant change in the graphitic content as well as the C=O functionalities (Figure 3.7a,b). Raman spectroscopy studies further revealed that the intensity ratio of D and G bands  $(I_D/I_G = 0.93)$  in case of pristine s-CDs did not change appreciably in the recovered s-CDs (Figure 3.7c). This revealed that the graphitic pool of s-CD is not affected during the reaction and the sulphonated groups play a significant role in the reaction kinetics. For further investigation into the role of surface acid functional groups on the catalytic activity for the C-C coupling reaction, a small amount of a base (1mL of a 500 mM aqueous NaOH solution) was added in the



*Figure 3.5. a) TEM study of the recovered s-CDs after the fourth cycle, b) Normalized fluorescence emission spectra of the pristine of recovered s-CDs, c) FTIR spectra of s-CDs and recovered s-CDs after fourth cycle of reactions.* 

Catalyst	C	Н	0	S	Adsorbed H <sub>2</sub> O
Wt % in s-CD	50.2	4.64	33.6	2.3	9.26
Atom ratio	4.2	4.64	2.1	0.0718	0.514
Wt % in	52.3	3.7	32.6	2.12	9.28
Recycled s-CD					
Atom ratio	4.36	3.7	2.04	0.066	0.515

Table 3.5. Elemental analysis of s-CDs

reaction mixture of the model coupling reaction. The conversion of the coupling product was reduced to 25% under visible-light illumination. This suggests the effect of deprotonating the acid sites present on the catalyst surface on the catalytic activity. Furthermore, the s-CDs were thermally treated at 200 °C, which results in the reconstitution of the graphitic core and removal of some of the surface functional groups, as confirmed by elemental analysis (Table 3.6). The catalytic activity of the resultant s-CD for the coupling reaction is greatly reduced (17%) suggesting that the acidic functional groups of the carbon dots play a



**Figure 3.6.** a) The high resolution XPS spectra of S2p region in s-CD revealed the peaks at 164.7 eV for sulfoxide and 169.7 eV for sulphonic acid and sulphate, b) The S2p core level XPS spectra of recycled s-CDs show that the amount of SO<sub>3</sub>-H functionality (169.7 eV) is reduced in the recovered s-CDs as compared to the pristine ones.

**Table3.6.** Elemental analysis of s-CDs obtained after thermal treatment at 200  $\degree$  C

Catalyst	C	Н	0	S	Adsorbed H <sub>2</sub> O
Wt % in s-CD	53.6	3.9	31.2	0.93	10.37
Atom ratio	4.46	3.9	1.95	0.015	0.576

major role in the formation of the coupling product.

#### 3.2.4 Mechanistic Investigation

Following earlier reports,<sup>[25-27]</sup> a two-step mechanism is suggested for the C-C coupling reaction, where the first step involves oxidation of xanthene to form a peroxo intermediate, which undergoes acid-catalyzed substitution of peroxide group by nucleophiles to form the final product. In order to substantiate the mechanistic pathway in the visible-light enhanced coupling reaction, a control reaction of 2-methoxyxanthene and cyclohexanone was performed under O<sub>2</sub> atmosphere (Scheme 3.2a). We can observe the *in situ* formed hydroperoxide intermediate by stopping the reaction after 2 hours, which can be isolated and structurally confirmed by <sup>1</sup>H-NMR and HRMS. The hydroperoxide intermediate subsequently converts to the desired coupling product. This suggests the dual role of s-CD as both oxidative as well as acidic properties in the catalyst were in



Figure 3.7. a) The deconvoluted XPS spectra of C1s region of s-CD, b) The deconvoluted C1s core XPS spectra of the recovered s-CDs, c) The Raman spectra of s-CD (red) and recovered s-CDs (blue) exhibited two broad peaks at D band and G band at owing to the in plane vibration of  $sp^2$  carbons.



Scheme 3.2. Formation of hydroperoxide intermediate followed by C-C coupling product.

operation. The oxidizing activity of  $-SO_3H$  groups on s-CD is responsible for the formation of xanthene hydroperoxide intermediate, whereas the acidic functionalities on the s-CD surface catalyzed the formation of the final coupling product from the xanthene hydroperoxide intermediate. Furthermore, based on this mechanism, the formation of H<sub>2</sub>O<sub>2</sub> is imminent (Scheme 3.2b). When 2-

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methoxyhydroperoxide intermediate was reacted with cyclohexanone under thermal conditions (at 50°C) for 30 min, the formation of  $H_2O_2$  was detected by iodometric method and monitored by UV-visible spectroscopy (Figure 3.8a). The results suggest the possibility of involvement of the *in situ* generated  $H_2O_2$  as an oxidant for the coupling reaction. Surprisingly, even the presence of catalase as a  $H_2O_2$  scavenger in the reaction medium did not have any impact on the yield of the coupling product (86 %) (Table 3.1).

It is worth mentioning that the oxidation step (conversion of benzylic hydrocarbon to give the hydroperoxide intermediate) can also be achieved in absence any catalyst through an auto-oxidation process under oxygen environment, however the reaction takes a longer time.<sup>[34]</sup> Thus the use of a strong acid such as PTSA or H<sub>2</sub>SO<sub>4</sub> as catalysts required a much longer reaction time, as only the coupling step is catalysed by the acids. Thus, it is apparent that the photocatalytic activity of s-CDs was greatly influential towards enhanced activity and selectivity for the cross-dehydrogenative coupling reaction even in comparison with their two-dimensional counterpart s-GO. In case of s-GO as the catalyst, we observed that the selectivity for the coupling reaction was rather poor and the oxidized product xanthenone was formed as a byproduct with a significant amount, although the acid surface-functionalized GO are known to demonstrate both oxidizing as well as acidic properties.<sup>[6]</sup> Even s-CDs, show much lower selectivity for the coupling product when the reactions were carried out under thermal conditions (70 °C, Table 3.1, entry 3 and Table 3.2, Entry 8). We and others<sup>[5-6]</sup> have earlier demonstrated that the oxidizing and acidic properties of various carbonaceous catalysts originated from the acid functionalities present on the surface. As the same surface functional groups participate in both steps in a consecutive reaction (oxidation and acidic steps), there might be a possibility for reduction in acid functionalities during the oxidation process. The inability of the catalytic system to create sufficiently stronger acidic environment might hamper the formation of the desired C-C coupling product and the oxidized product is also obtained in a significant amount. FTIR studies of s-GO nanocatalysts recovered after one cycle of the model coupling reaction showed a slight decrease in intensity for the acid functional groups (Figure 3.8b).





*Figure 3.8. a*) *UV/Visible absorption spectra of the tri-iodide formed by*  $H_2O_2$  *oxidation, b*) *Normalized FTIR spectra of fresh s-GO (red) and s-GO after one cycle of reaction (pink).* 



**Figure 3.9.** a) Free radical scavenging experiment, using a mixture of xanthene, 2methoxyxanthenehydroperoxide and cyclehexanone; (b) effect of various radical scavengers on the photocatalytic C-C coupling reaction; (c) DMPO trapped EPR spectra resulting from DMPO binding with superoxide radicals ( $O_2^-$ ).

On the other hand, earlier reports suggested an enhancement of the surface acidity of the sulphonated carbon dots (s-CD) under light irradiation.<sup>[35]</sup> For the coupling step, the enhanced surface acidity probably plays an important role in the selectivity of the coupling product formation.

It appears from the data in Table 3.1 that the rate of the coupling reaction on the s-CD surface can be substantially enhanced under visible light irradiation; we next investigated the involvement of free radicals in the reaction pathway. A

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few controlled reactions were carried out using a mixture of xanthene (1), 2methoxyxanthenehydroperoxide (X) and cyclohexanone and the product formation was monitored in the presence of free radical scavengers under visiblelight irradiation (Figure 3.9a). Upon addition of butylated hydroxytoluene (BHT), **3ac** was obtained in 85% yield, while 90% of **1** was recovered. This suggests that radical species are involved in the oxidation of xanthene to its hydroperoxide and the Bronsted acid catalyzed substitution of the peroxide group by nucleophiles was not affected by the radical scavenger. In order to understand the specific radical involved in the oxidation pathway, we performed a series of control experiments (Figure 3.9b). When an 'OH radical scavenger, tert-butyl alcohol (TBA), was added, no effect on the conversion was observed. However, upon the addition of p-benzoquinone (BQ) as an  $O_2^-$  scavenger to the photocatalytic reaction, a reduced conversion (17%) was noted. The results suggest the possible role of  $O_2^-$  radicals in the *in situ* generation of hydroperoxide intermediate. Further, we employed a spin trapping electron paramagnetic resonance technique using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as probe to detect the superoxide radical formed over the s-CD surface during the reaction. As expected, we observed characteristic fingerprint of spin adducts resulting from the superoxide radical in the EPR signal (Figure 3.8c). While the addition of EDTA-2Na as a hole (h<sup>+</sup>) scavenger has no effect on the reaction, the addition of CuCl<sub>2</sub> as an electron (e) scavenger in the photocatalytic reaction resulted in reduced conversion (26%), suggesting electron transfer during oxidation. Next, we explored the photoinduced electron transfer properties of s-CDs, which were confirmed by observing the emission quenching in the presence of either electron acceptor or electron donor molecules in solution under visible light irradiation.

When a known electron acceptors 2, 4-dinitrotoluene (DNT, 0.9 V vs NHE) or electron donor N, N-diethylaniline (DEA, 0.88 V vs NHE)<sup>[36]</sup> was added to the s-CD aqueous solution, its emission intensity at 424 nm was efficiently quenched. The Stern-Volmer quenching constants ( $K_{sv} = \tau_{F^0}kq$ ) were calculated from the linear regression and found to be 0.4619 mM<sup>-1</sup> and 2.53 M<sup>-1</sup> for DNT and DEA, respectively (Figure 3.10 a, b). The transient photocurrent experiment further revealed the formation of electron-hole pairs during visible light exposure (Figure 3.9c). Kubelka-Munk-transformed reflectance spectrum of

s-CD was used to evaluate the optical band gap, which was found to be 2.55 eV. Cyclic-voltametry experiments revealed the lowest unoccupied molecular orbital (LUMO) of s-CD at -0.68 V vs Hg/HgCl<sub>2</sub> (Figure 3.10). The corresponding highest occupied molecular orbital (HOMO) level is calculated by subtracting the LUMO level from the optical band gap, and a value of +1.87 V indicates a high oxidizing nature of s-CD.



**Figure 3.10.** a) Electron acceptor 2,4-dinitrotoluene (DNT, 0.9 V vs NHE) in toluene were added to the s-CD aqueous solution, b) Electron donor N, N-diethylaniline (DEA, 0.88 V vs NHE) in methanol were added to the aqueous s-CD solution and the calculated Stern-Volmer quenching constants were found to be 2.53  $M^{-1}$ , c) Transient photocurrent response of s-CDs under visible light.

Based on the experimental results, a photocatalytic mechanism for the C–C coupling reaction is proposed (Scheme 3.3). Upon visible light irradiation, the excitation of electrons from the HOMO in the s-CD framework generates reductive electrons and oxidative holes. The effective electron transfer from the LUMO of s-CD to  $O_2$  results in the formation of superoxide radical ( $O_2^-$ ) which reacts with the benzylic position of xanthene to give the hydroperoxide intermediate. This is followed by the formation of a highly stabilized carbocation



Figure 3.11. (a) Band gap of s-CD obtained from UV-Visible spectrum and calculated using Kubelka-Munk theory; (b) Reduction potential of s-CD measured by cyclic voltammetry; (c) HOMO/LUMO band positions of s-CD; (d) Cyclic voltamograms of the s-CDs/ITO electrode in acetonitrile using lithium perchlorate (LiClO<sub>4</sub>) as an electrolyte under visible light irradiation or without light irradiation.



*Scheme 3.3.* Proposed Mechanism for Photoinduced CDC Reaction of Benzylic Hydrocarbon and Ketone Using s-CD as Photocatalyst in presence of  $O_2$ .

with the release of  $H_2O_2$ , driven by a stronger acidic environment resulting from the ionization of surface -SO<sub>3</sub>H groups. Finally, the enol form of cyclohexanone couples with the carbocation to give the desired product. Furthermore, the release of additional protons from the ionization of -SO<sub>3</sub>H groups on the s-CD surface under visible light irradiation creates a stronger acidic environment,<sup>[36]</sup>which might enhance the conversion and selectivity of hydroperoxide intermediates to the desired coupling product.

## 3.3 Conclusion

In summary, we demonstrate that s-CDs can act as a high performance visible-light induced photocatalyst for the aerobic oxidative coupling of xanthenes (or thioxanthenes) with a variety of nucleophiles such as ketones, 1, 3dicarbonyls and arenes under mild reaction conditions. The s-CDs demonstrate dual catalytic properties that include photoactivation of benzylic -CH<sub>2</sub> groups in xanthenes in presence of  $O_2$  resulting in the formation of hydroperoxy intermediate, followed by coupling of the nucleophiles catalyzed by acid surface functionalities. In case of carbon dots, the photocatalytic activity can be tailored through proper surface engineering with various surface functionalities, for example, in -C=O and -COOH terminated carbon dots, hole transportation towards surface is more favourable than electron/hole pair recombination thus resulting in high photocatalytic activity. Furthermore, the carbon dot surfaces can be easily modified or conjugated to various other functionalities to divulge multicatalytic sites on the same heterogeneous entity. The high efficiency and selectivity of the coupling reaction in a short time period under visible-light irradiation clearly demonstrate that these tiny carbonanceous materials can be used for multi-step organic transformations in a one-pot synthesis. Several advantages, such as easy synthesis from cheap precursors, biocompatibility, recyclability, possibility of integrating catalytically active entities on the surface and inherent enzyme-mimetic activities can make carbon dots a green alternative to metal catalysts for various multi-step organic synthesis.

## **3.4 Experimental Section**

## 3.4.1 Materials

Glucose, oleic acid, oleum, catalase, 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and all other chemicals were purchased from Sigma-Aldrich, India or Merck, India and used without further purification. We used Millipore water (ultrapure level) throughout the experiments.

## 3.4.2 Synthesis of carbon dots

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First the Carboxyl functionalized Carbon dots (c-CDs) were synthesized in large scale by following a previously reported procedure<sup>[37]</sup> with slight modification. 5.0 g of glucose in 10 ml of oleic acid was subjected to microwave irradiation using a focused microwave CEM discover reactor at 150 W and 180 °C for 7 min. The resultant solid brownish product was dispersed in water and hexane was used several times to extract the excess oleic acid. Finally the product was purified by dialyzing against ultra-pure water for 24 h to remove any excess precursor. 3.2 g of c-CDs were obtained as solid product after removal of water using lyophilizer.

The  $-OSO_3H$  functionalized carbon dots (s-CD) were synthesized by treating c-CDs (1g) with fuming sulphuric acid (40 ml) at room temperature for 72 h under nitrogen environment to give a dark coloured suspension. The suspension was added into anhydrous diethyl ether with vigorous stirring in an ice bath. The precipitates were separated from the solution through centrifugation and washed by water and ethanol.

#### 3.4.3: Synthesis of Graphene oxide

Graphene oxide (GO) were synthesized from graphite powder by modified Hummer's method as reported earlier <sup>[38]</sup> and was purified by dialyzing against ultra-pure water for 24 h to remove any metal impurity. The  $-SO_3H$  groups where introduced by treating graphene oxide (500 mg) with fuming sulphuric acid (20 ml) at room temperature for 72 h under a nitrogen environment to prepare s-GO.

#### 3.4.4 Quantitative Measurement of functional groups on the s-CD surface

A quantitative estimation of hydroxyl, carboxyl, sulfonic functionality on the s-CD surface was evaluated following an earlier report.<sup>[39]</sup> First the concentration of the functional groups was evaluated by treating a 5.0 mL aqueous solution containing s-CDs (1.0 mg/mL concentration) with NaOH (0.05 mol/L) for 60 min at 25 °C in an ultrasonic bath. After the removal of s-CDs by centrifugation, the supernatant was titrated against aliquots of aqueous HCl (0.05 mol/L) using phenolphthalein as an indicator. The concentration of functional groups was calculated to be  $2.2 \times 10^{-3}$  mol/L.

For the measurement of carboxyl and sulfonic functional groups, a similar

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method was adopted except for treating a 5 mL aqueous dispersion of s-CDs (1 mg/mL concentration) with sodium bicarbonate (0.05mol/L). The supernatant was titrated against aqueous HCl (0.05 mol/L) using phenolphthalein as an indicator. The concentration of -COOH and -OSO<sub>3</sub>H functional groups was found to be  $0.9 \times 10^{-3}$  mol/L. Similarly, for the measurement of -OSO<sub>3</sub>H functional groups, the s-CD catalyst was stirred with NaCl (0.05 mol/L) and the supernatant was titrated against the sodium hydroxide (0.05 mol/L) using phenolphthalein as an indicator. The concentration of -OSO<sub>3</sub>H functional groups was found to be 0.4  $\times 10^{-3}$  mol/L. All the measurements were repeated thrice to ascertain precision. From the measurements, the concentration of -OH, -COOH and -OSO<sub>3</sub>H on the s-CD surface was calculated to be  $1.3 \times 10^{-3}$  mol/L,  $0.5 \times 10^{-3}$  mol/L and  $0.4 \times 10^{-3}$  mol/L respectively. The surface functional group measurements were also carried out for the s-CDs recovered after the catalytic cycles.

Similarly, the concentration of surface functional groups on graphene oxide (GO) and sulphonated graphene oxide (s-GOs) were quantified by acidbase titration. The carboxyl and hydroxyl group concentration was found to be  $1.86 \times 10^{-4}$  mol/L and  $1.94 \times 10^{-3}$  mol/L respectively in an aqueous solution of 1 mg/mL concentration of GO. Similarly, the carboxyl, hydroxyl and sulfonic group concentration was found to be  $1.8 \times 10^{-4}$  mol/L and  $1.73 \times 10^{-3}$  mol/L and  $1.65 \times 10^{-4}$  mol/L respectively in an aqueous solution of 1 mg/mL concentration of s-GO.

#### 3.4.5 Photocatalytic C-C coupling of benzylic hydrocarbon with ketones

In a typical reaction, 0.5 mmol of the hydrocarbon substrate, 6 equivalents of cyclohexanone and 5 mg of s-CD were taken in a tube, where cyclohexanone acted as both reactant and solvent. The photocatalytic reactions were performed using a 34 watt blue LED lamp (hv=425 nm) at room temperature under O<sub>2</sub> environment. Magnetic stirring was performed throughout the reaction. The progress of the reaction was monitored by TLC using ethyl acetate and hexane as eluent. After completion of the reaction, the resulting mixture was extracted with ethyl acetate (3 x 20 ml) and washed with water (1 x 15 ml). The organic layer was dried over anhydrous sodium sulphate and evaporated under reduced pressure to get the residue. The residue was purified using silica gel column

chromatography (100-200 mesh) where a mixture of hexane and ethyl acetate was used as the eluent.

#### 3.4.6 Synthesis of N-phenyl-tetrahydroisoquinoline



Phenyl boronic acid (0.368g, 2 mmol) and Cu(OAc)<sub>2</sub>.H<sub>2</sub>O (20 mg, 0.1 mmol) in DCM (10 mL) were taken in a flask and the mixture was stirred for 5 minutes at room temperature. To this stirring suspension was added 1,2,3,4 tetrahyroisoquinoline (0.072 g, 99.0  $\mu$ L 1 mmol) and stirred under O<sub>2</sub> atmosphere for 24 h. The mixture was extracted with water and DCM. The product was purified using silica gel column chromatography (using 2% ethylacetate/ hexane). **3.4.7 Synthesis of Thioxanthene** 



THF, reflux at 60°C, 12 hrs

In the typical synthesis of thioxanthene, 5 mmol of thioxanthenone was dissolved in 40 ml of dry THF and added into it 1.2 equivalents of NaBH<sub>4</sub> and 6 mmol of I<sub>2</sub> at 0 °C. After bringing to room temperature, the reaction mixture was refluxed for 12 h at 60 °C. The reaction mixture was quenched with brine and extracted with ethyl acetate. The organic layer was separated, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under vacuum. The crude residue was purified using column chromatography on silica gel (eluting with 2% ethylacetate / hexane) to provide thioxanthene with 92% yield.

#### 3.4.8 Leaching experiment

The model coupling reaction of xanthene and cyclohexanone was carried out under visible light illumination under optimal reaction conditions. The reaction was stopped after 90 min (approx. 50% conversion) and the s-CD catalyst were removed from the reaction mixture by centrifugation. The reaction was further continued with the supernatant for 10 h under visible light irradiation.

### 3.4.9 Recyclability studies of s-CDs

To study the recyclability of s-CDs, the model photocatalytic reaction was performed in cycles of reactions under standard photocatalytic reaction conditions. After the completion of the  $1^{st}$  cycle of the reaction, the organic products were extracted using ethyl acetate, while the s-CDs were separated out by centrifugation. The  $2^{nd}$  cycle of the photocatalytic reaction was carried out using the recovered s-CDs as catalyst. The same s-CDs could be reused for at least for four runs with excellent yields. The s-CDs showed efficient recyclability as a photocatalyst and 76% of the desired coupling product could be obtained even after the fourth cycle.

#### 3.4.10 Detection of hydrogen peroxide in the catalytic reactions

To detect  $H_2O_2$  during the catalytic reaction, a modified iodometric method was employed. After 15 minutes of the reaction between 2methoxyhydroperoxide intermediate with cyclohexanone under thermal condition (at 50°C), an equal volume of water and dichloromethane was added to extract the formed coupling product. The aqueous layer was acidified with  $H_2SO_4$  to pH  $\approx 2$  and 1 mL of a 10% solution of KI and three drops of 3% solution of ammonium molybdate were added. In the presence of hydrogen peroxide I<sup>-</sup> is oxidised to I<sub>2</sub>,  $H_2O_2 + 2\Gamma + 2H^+ \rightarrow 2H_2O + I_2$ , and with an excess of iodide ions, the tri-iodide ion is formed according to the reaction I<sub>2</sub> (aq.) +  $\Gamma \rightarrow I^{3-}$ .The formation of I<sup>3-</sup> could be monitored by UV-Visible spectroscopy at wavelength 353 nm.

#### 3.4.11 Characterization data

## 3.4.11.1 Characterization data of synthesized coupling products

**2-(9H-xanthen-9-yl)cyclopentanone (3aa):** Colourless solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.29-7.22 (m, 3H), 7.15-7.10 (m, 4H), 7.02 (t, *J* = 7.4 Hz, 1H), 4.79 (d, *J* = 2.7 Hz, 1H), 2.47 (td, *J* = 9.7 Hz, *J* = 2.2 Hz, 1H), 2.27 (dd, *J* = 18.5 Hz, *J* = 7.4 Hz, 1H), 1.84-1.76 (m, 2H), 1.69-1.63 (m, 1H), 1.61-1.51 (m, 1H), 1.44 (ddd, *J* = 23.3 Hz, *J* = 11.3 Hz, *J* = 6.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 199.4, 153.1, 152.5, 129.2, 128.2, 127.8, 124.5, 123.7, 123.5, 121.9; 116.4, 116.3, 59.9, 39.3, 38.0, 24.0, 20.4 HR-MS (ESI positive) m/z: calcd. For C<sub>18</sub>H<sub>16</sub>O<sub>2</sub>Na<sup>+</sup>, [M+Na]<sup>+</sup>: 287.135551; found: 315.135314.

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**2-(9H-xanthen-9-yl)cyclohexanone (3ab):** Colourless solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.42 (dd, J = 7.52 Hz, 1H), 7.23-7.17 (m, 3H), 7.07-7.0 (m, 4H), 4.93 (s, 1H), 2.52-2.39 (m, 2H), 2.27-2.19 (m, 1H), 1.94-1.91 (m, 1H), 1.77-1.69 (m, 2H), 1.48-1.40 (m, 2H), 1.14-1.04 (m, 1H), 1.55-1.41 (m, 2H), 1.15 (ddd, J = 25.6 Hz, J = 12.8 Hz, J = 3.6 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 210.8, 153.3, 153.0, 130.5, 128.8, 127.8, 127.7, 125.6, 123.5, 123.2, 122.9, 116.3, 116.1, 60.7, 42.1, 36.7, 26.7, 24.8, 23.1; HR-MS (EI) m/z: calcd. for C<sub>19</sub>H<sub>18</sub>O<sub>2</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 301.130678; found: 301.130632.

**9-(2,4-dimethoxyphenyl)-4-methoxy-9H-xanthene (3ac)**: White solid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 7.20 (d, J= 8.4 Hz, 1H), 7.13 (dt, J=8.4 Hz, 1H), 7.08 (d, J= 7.64 Hz, 1H), 6.91 (dt, J= 7.6 Hz, 1H), 6.85 (t, J= 7.64 Hz, 1H), 6.82 (d, J= 8.4 Hz, 1H), 6.75 (d, J= 7.64 Hz, 1H), 6.70 (d, J= 7.64 Hz, 1H), 6.43 (s, 1H), 6.32 (dd, J= 8.4 Hz, 1H), 5.69 (s, 1H), 3.91 (s, 3H), 3.80 (s, 3H), 3.70 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 210.1, 153.2, 152.9, 147.9, 147.8, 142.8, 142.6, 130.4, 128.7, 127.7, 127.6, 126.6, 125.6, 123.9, 123.7, 123.4. 123.2, 122.8, 122.7, 122.2, 120.4, 116.7, 116.7, 116.6, 110.2, 110.0, 60.5, 56.2, 56.1, 42.13, 42.09, 36.8, 36.7, 29.7, 29.7, 27.8, 27.5, 26.7, 26.6, 24.74, 24.72; HR-MS (EI) m/z: calcd. for C<sub>20</sub>H<sub>20</sub>O<sub>2</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 301.150668; found: 301.150652.

**2-(2-hydroxy-9H-xanthen-9-yl)cyclohexanone** (**3ad**): Yellow solid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ (ppm): 7.42 (dd, J = 7.52 Hz, 1H), 7.23-7.17 (m, 3H), 7.07-7.0 (m, 2H), 6.99-6.92 (m,3H), 4.93 (s, 1H), 2.52-2.39 (m, 2H), 2.27-2.19 (m, 1H), 1.94-1.91 (m, 1H), 1.77-1.69 (m, 2H), 1.48-1.40 (m, 2H), 1.14-1.04 (m, 1H), 1.55-1.41 (m, 2H), 1.15 (ddd, J = 25.6 Hz, J = 12.8 Hz, J = 3.6 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 210.8, 153.3, 153.0, 130.5, 128.8, 127.8, 127.7, 125.6, 123.5, 123.2, 122.9, 116.3, 116.1, 60.7, 42.1, 36.7, 26.7, 24.8, 23.1; HR-MS (EI) m/z: calcd. for C<sub>19</sub>H<sub>18</sub>O<sub>3</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 317.120568; found: 317.120343.

**2-(9H-xanthen-9-yl)cycloheptanone** (**3ae**): Colourless solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.26-7.20 (m, 3H), 7.10-7.04 (m, 4H), 7.01 (t, *J* = 7.3 Hz, 1H), 4.64 (d, *J* = 3.9 Hz, 1H), 2.5 (d, *J* = 11.4 Hz, 1H), 2.36-2.32 (m, *J* = 12.4 Hz,1H), 2.16-2.06 (m, 1H), 1.74-1.72 (br m, 3H), 1.38-1.12 (m, 4H), 1.05-0.99 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 216.4, 153.2, 153.0, 129.1, 128.7, 128.1, 127.9, 124.5, 123.6, 123.1, 121.9, 116.6, 116.3, 62.4, 44.7, 42.1,

29.9, 28.5, 25.1, 24.8. HR-MS (ESI positive) m/z: calcd. For C<sub>20</sub>H<sub>20</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup>: 315.135551; found: 315.135314.

**2-(9H-thioxanthen-9-yl)cyclohexanone** (**3ba**): Light yellow solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.63 (dd, J = 7.56 Hz, J = 1.68 Hz, 1H), 7.42-7.36 (m, 2H), 7.24-7.10 (m, 6H), 4.69 (d, J = 9.52 Hz, 1H), 3.14-3.07 (m, 1H), 2.35-2.30 (m, 1H), 2.22-2.14 (m, 1H), 2.01-1.94 (m, 1H), 1.76-1.69 (m, 1H), 1.63-1.50 (m, 3H), 1.40-1.32 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 212.1, 141.9, 138.6, 136.6, 133.7, 132.7, 130.9, 130.2, 127.2, 126.6, 126.4, 126.2, 50.4, 47.3, 43.2, 33.9, 29.8, 28.9, 25.3; HR-MS (ESI positive) m/z: calcd. For C<sub>19</sub>H<sub>18</sub>NaOS [M+Na]<sup>+</sup>: 317.095651; found: 315.09311.

**2-(9H-thioxanthen-9-yl)cycloheptanone (3bb):** White soild, <sup>1</sup>*H* NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.42-7.36 (m, 1H), 7.28-7.27 (m, 1H), 7.24-7.10 (m, 5H), 4.50 (d, *J* = 10.2 Hz, 1H), 2.31-2.23 (m, 1H), 2.10-2.04 (m, 1H), 2.16-2.06 (m, 1H), 1.76-1.66 (br m, 3H), 1.50-1.44 (m, 1H), 1.38-1.34 (m, 1H), 1.24 (br s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 214.5, 136.9, 135.8, 133.4, 132.6, 130.5, 130.3, 127.3 (t), 127.0, 126.7, 126.45, 126.41, 126.1, 50.9, 50.0, 43.7, 29.7, 28.4, 27.8, 23.6; HR-MS (ESI positive) m/z: calcd. For C<sub>20</sub>H<sub>20</sub>NaOS [M+Na]<sup>+</sup>: 332.115851; found: 332.114113.

**3-(9H-xanthen-9-yl)pentan-2-one (3ca):** Brown oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.27-7.21 (m, 2H), 7.15-7.02 (m, 6H), 4.08 (d, J = 8.5 Hz, 1H), 2.69 (t, J=10.8 1H), 1.76 (s, 3H), 1.62-1.55 (m, 1H), 1.39-1.33 (m,1H), 0.73 (t, J = 7.3 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 212.2, 153.2, 129.6, 128.8, 128.1, 127.9, 124.7, 124.1, 123.5, 123.1, 116.7, 61.0, 42.8, 33.4, 22.9, 12.0; HR-MS (EI) m/z: calcd. for C<sub>18</sub>H<sub>18</sub>O<sub>2</sub> [M+Na]<sup>+</sup>: 289.120678; found: 266.120632.

**1-phenyl-2-(9H-xanthen-9-yl)ethanone** (**3cb**): White solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.79 (d, J = 5.4 Hz, 2H), 7.48 (t, J = 8.04 Hz, 1H), 7.37-7.30 (m, 4H), 7.19 (t, J = 7.8 Hz, 2H), 7.1 (d, J = 6.84 Hz, 2H), 7.02 (t, J = 5.6 Hz, 2H), 4.85 (t, J = 4.4 Hz, 1H), 3.34 (d, J = 5.1 Hz, 2H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 197.2, 152.3, 129.5, 128.8, 128.5, 128.1, 127.9, 126.3, 125.5, 123.5, 116.6, 57.1, 43.3; HR-MS (ESI positive) m/z: calcd. for C<sub>21</sub>H<sub>16</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup>: 323.104136; found: 323.104250.

**1-phenyl-2-(9H-xanthen-9-yl)propan-1-one (3cc):** Pale yellow oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.67 (d, *J* = 7.28 Hz, 2H), 7.41 (t, *J* = 7.52 Hz, 1H),

7.30 (t, J = 7.7 Hz, 2H), 7.19 (td, J = 8.5 Hz, J = 1.5 Hz, 1H), 7.11(d, J = 7.5 Hz, 1H), 7.09-6.96 (m, 5H), 6.85(td, J = 7.5 Hz, J = 2.0 Hz,1H), 4.32 (d, J = 7.7 Hz, 1H), 3.64-3.57 (m, 1H), 1.18 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 203.4 , 153.4, 153.1, 137.1, 129.9, 129.0, 128.6, 128.2, 127.9 , 125.2, 123.6 , 116.58, 116.62, 68.4, 48.6, 42.8, 29.8, 14.6 HRMS (ESI positive) m/z: calcd. for C<sub>22</sub>H<sub>18</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup>: 337.119729; found: 337.119576.

**1-(p-tolyl)-2-(9H-xanthen-9-yl)propan-1-one (3cd):** Yellow oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 7.66 (d, J = 7.7 Hz, J = 1.4 Hz, 2H), 7.26 (t, J = 9.0 Hz, 1H), 7.19-7.03 (m, 8H), 6.92 (td, J = 6.4 Hz, J = 1.5 Hz, 1H), 4.40 (d, J = 7.6 Hz, 1H), 3.68-3.61 (m, 1H), 2.34 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm): 202.1 , 173.5, 165.4, 159.4, 157.3, 151.5, 130.8, 129.5, 128.1, 127.5, 125.1 , 123.0, 123.3 , 116.7, 104.9, 98.8, 55.6, 55.3, 36.4, 31.0 HRMS (ESI positive) m/z: calcd. for C<sub>23</sub>H<sub>20</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup>: 351.139789; found: 333.139578.

**1-phenyl-2-(9H-thioxanthen-9-yl)ethanone (3da):** Colourless oil,<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.80 (d, *J* = 5.3 Hz, 2H), 7.49 (t, *J* = 8.01 Hz, 1H), 7.36-7.32 (m, 4H), 7.20 (t, *J* = 7.8 Hz, 2H), 7.1 (d, *J* = 6.84 Hz, 2H), 7.03 (t, *J* = 5.6 Hz, 2H), 4.86 (t, *J* = 4.4 Hz, 1H), 3.34 (d, *J* = 5.1 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 198.1, 152.2, 129.4, 128.6, 128.4, 128.2, 127.7, 126.3, 125.5, 123.5, 116.5, 57.1, 43.3; HRMS (ESI positive) m/z: calcd. for C<sub>21</sub>H<sub>16</sub>NaOS [M+Na]<sup>+</sup>: 339.073724; found: 339.070572.

**dimethyl 2-(9H-xanthen-9-yl)malonate (3ea):** Yellow oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.30 (dd, J = 7.6 Hz, J = 1.6 Hz, 2H), 7.25 (td, J = 8.1 Hz, J = 1.7 Hz, 2H), 7.15 (dd, J = 8.2 Hz, J = 1.1 Hz, 2H), 7.05 (td, J = 7.4 Hz, J = 1.2 Hz, 2H), 4.82 (d, J = 9.0 Hz, 1H), 3.6 (d, J = 9.0 Hz, 1H), 3.55 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 167.6, 152.7, 129.1, 128.9, 123.4, 122.7, 116.9, 60.0, 52.5, 39.9; HR-MS (ESI positive) m/z: calcd. for C<sub>18</sub>H<sub>16</sub>NaO<sub>5</sub> [M+Na]<sup>+</sup>: 335.088992; found: 335.088817.

diethyl 2-(9H-xanthen-9-yl)malonate (3eb): Brown oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.32 (dd, J = 7.6 Hz, J = 1.5 Hz, 2H), 7.26-7.22 (m, 2H), 7.14 (dd, J = 8.2 Hz, J = 1.04 Hz, 2H), 7.05 (td, J = 7.4 Hz, J = 1.2 Hz, 2H), 4.81 (d, J = 8.9 Hz, 1H), 4.06-3.94 (m, 2H), 3.59 (d, J = 8.9 Hz, 1H), 1.08 (t, J = 7.2 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 167.5 , 153.2, 129.0, 128.5, 123.4, 122.9, 116.7, 61.6, 60.3, 39.7, 13.5; HR-MS (ESI positive) m/z: calcd. for C<sub>20</sub>H<sub>20</sub>NaO<sub>5</sub> [M+Na]<sup>+</sup>: 363.117982; found: 335.117812.

ethyl 3-oxo-2-(9H-xanthen-9-yl)butanoate (3ec): Yellow oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.33 (dd, J = 7.7 Hz, J = 1.4 Hz, 1H), 7.27-7.24 (m, 3H), 7.14 (ddd, J = 8.5 Hz, J = 4.1 Hz, J = 1.3 Hz, 2H), 7.04 (m, 2H), 4.85 (d, J = 9.2 Hz, 1H), 4.03-3.94 (m, 2H), 3.79 (d, J = 9.2 Hz, 1H), 1.90 (s, 3H), 1.09 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 201.8 , 167.4, 153.4, 153.3, 129.7, 129.3, 128.49, 128.47, 123.6 (t), 123.5 123.4, 123.3 , 116.9, 116.7, 63.9, 60.3, 39.5, 32.9, 13.9; HRMS (ESI positive) m/z: calcd. for C19H18NaO4 [M+Na]<sup>+</sup>: 333.109729; found: 333.109576.

**dimethyl 2-(9H-thioxanthen-9-yl)malonate (3fa):** Light yellow solid,<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.44-7.42 (m, 2H), 7.40-7.38 (m, 2H), 7.20-7.19 (m, 4H), 4.91 (d, *J* = 9.04 Hz, 1H), 4.2 (d, *J* = 9.04 Hz, 1H), 3.47 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 167.7, 153.2, 134.3, 133.5, 130.0, 127.3, 126.5, 52.4, 51.4, 48.7; HR-MS (ESI positive) m/z: calcd. for C<sub>18</sub>H<sub>16</sub>NaO<sub>4</sub>S [M+Na]<sup>+</sup>: 351.078972; found: 351.078816.

diethyl 2-(9H-thioxanthen-9-yl)malonate (3fb): Light yellow oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.44-7.41 (m, 4H), 7.20-7.18 (m, 4H), 4.82 (d, *J* = 8.9 Hz, 1H), 4.91 (d, *J* = 8.8 Hz , 1H), 4.16 (d, *J* = 8.9 Hz, 1H), 3.99-3.87 (m, 4H) 1.03 (t, J= 5.84, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 167.5, 153.4, 134.5, 133.6, 130.2, 127.2, 126.5, 61.3, 51.5, 48.7, 13.8; HR-MS (ESI positive) m/z: calcd. For C<sub>20</sub>H<sub>20</sub>NaO<sub>4</sub>S [M+Na]<sup>+</sup>: 379.097282; found: 363.097132.

methyl 3-oxo-2-(9H-thioxanthen-9-yl)butanoate (3fc): White solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 7.43-7.40 (m, 3H), 7.34 (m, 1H), 7.20-7.18 (m, 4H), 4.93 (d, J = 11.0 Hz, 1H), 4.46 (d, J = 10.76 Hz, 1H), 3.97-3.88 (m, 2H), 1.82 (s, 3H), 1.05 (t, J = 7.01 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm): 201.9, 167.4, 134.7, 134.4, 133.9, 133.44, 133.39, 130.6, 130.2, 127.3, 127.2, 127.1, 126.8, 126.6, 61.4, 57.5, 48.4, 31.2, 13.9; HRMS (ESI positive) m/z: calcd. for C<sub>18</sub>H<sub>16</sub>NaO<sub>3</sub>S [M+Na]<sup>+</sup>: 335.068572; found: 333.0684576.

**2-(isochroman-1-yl)cyclopentanone (3ga):** Yellow oil, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.34-7.20 (m, 4H), 4.35 (d, *J*= 7.6,1H), 3.75 (m, 2H), 2.77-2.70 (m, 3H), 2.10-1.85 (m, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 211.8, 137.1, 136.3, 127.5, 125.8, 125.7, 125.5, 77.5, 62.6, 54.7, 38.9, 28.6, 21.2, 14.1, HRMS (EI) m/z calcd for C<sub>14</sub>H<sub>16</sub>O<sub>2</sub> [M+Na]<sup>+</sup> 239.09380, found 231.09326.

**2-(isochroman-1-yl)cyclohexanone (3gb):** Yellow oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 7.23-7.14 (m, 3H), 7.13-7.09 (m, 1H), 7.01 (d, J=7.0 Hz, 1H),

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5.48 (s, 1H), 4.16 (dd, J=11.0, 5.4 Hz, 1H), 3.75 (t, J=11.3 Hz, 1H), 3.05-2.97 (m, 1H), 2.75 (dd, J=11.1, 5.6 Hz, 1H), 2.62-2.53 (m, 2H), 2.3-2.30 (m, 1H), 1.99 (dd, J=8.2, 4.8 Hz, 1H), 1.89-1.82 (m, 1H), 1.76 (ddd, J=32.4, 20.4, 12.8 Hz, 2H), 1.64 (d, J=7.1 Hz, 1H), 1.54 (t, J=12.5 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 210.8, 136.6, 135.5, 128.9, 126.3, 126.2, 123.9, 73.7, 64.3, 55.7, 42.0,29.3, 26.1, 25.2, 24.5 HRMS (EI) m/z calcd for C<sub>15</sub>H<sub>18</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 253.1180, found 253.1163.

**2-(isochroman-1-yl)cycloheptanone (gc):** Yellow oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.33 (m, 2H), 7.23 (m, 2H), 4.4 (d, J=10.9, 1H), 3.75-3.65 (m, 2H), 3.05 (m, 1H), 2.71 (m, 2H), 2.52-2.4 (m, 2H), 1.66-141.0 (m, 8H), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 214.6, 137.1, 136.3, 127.6, 125.8, 125.7,125.5, 78.0, 62.6, 54.6, 42.4, 29.5, 28.6, 26.7,24.2,22.7; HRMS (EI) m/z calcd for C<sub>15</sub>H<sub>18</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 253.1180, found 253.1163.

**2-(isochroman-1-yl)-1-phenylethanone** (**3ha**): Pale yellow oil, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 8.04 (d, *J*=7.17 Hz, 2H), 7.60-7.45 (m, 3H), 7.26-7.13 (m, 4H), 5.54 (d, *J*=8.7 Hz, 1H), 4.16-4.09 (m, 1H), 3.86-3.78 (m, 1H), 3.67-3.59 (m, 1H), 3.36-3.30 (m 1H), 3.08-2.98 (m, 1H), 2.76-2.69 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  (ppm): 198.1, 137.5, 137.1, 134.0, 133.1, 129.0, 128.5, 128.3, 126.5, 126.2, 124.5, 72.6,63.4, 45.4, 28.8; HRMS (EI) m/z calcd for C<sub>17</sub>H<sub>16</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 275.0923, found 275.0912.

**2-(isochroman-1-yl)-1-phenylpropan-1-one (3hb):** Yellow solid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 7.99-7.91 (m, 2H), 7.58-7.40 (m, 3H), 7.25-7.01 (m, 4H), 5.28-5.21 (m, 1H), 4.13-4.0 (m, 2H), 3.68-3.53 (m, 1H), 3.06-2.95 (m, 1H), 2.65-2.54 (m, 1H), 1.20-1.06 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>,75 MHz)  $\delta$  (ppm): 201.8, 177.2, 136.6, 135.8, 135.0, 132.7 (two peaks), 129.1, 128.7, 128.6, 128.5, 128.3, 126.6, 126.5, 126.3, 125.8, 124.5, 77.4, 76.6, 63.9, 63.3, 47.2, 46.7, 29.6, 28.8, 13.6, 9.7; HRMS (EI) m/z calcd for C<sub>18</sub>H<sub>18</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 289.11760, found 289.11742.

**2-(isochroman-1-yl)-1-(p-tolyl)propan-1-one** (**3hc**): Light yellow solid, diastereomeric ratio 2.9:1, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 7.87 (d, *J*= 8.4 Hz, 2H), 7.26 (d, *J*= 8.4 Hz, 2H), 7.16-7.08 (m, 4H), 5.26 (d, *J*= 3.8, 1H), 4.12-4.06 (m, 1H), 4.00-3.91 (m, 1H), 3.61-3.55 (m, 1H), 3.02-2.94 (m, 1H), 2.60-2.53 (m, 1H), 2.39 (s, 3H), 1.07 (d, *J*= , 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>,100 MHz)  $\delta$  (ppm):

201.5, 143.5, 143.4, 136.4, 135.1, 134.3, 129.4,129.2, 128.6, 126.6, 126.4, 124.6, 72.1, 70.4, 65.3, 64.0, 46.8, 34.3, 31.9, 29.5, 29.4, 29.3, 29.2, 28.9, 25.0, 22.7, 21.6, 14.2, 10.2; HRMS (EI) m/z calcd for  $C_{19}H_{20}NaO_2$  [M+Na]<sup>+</sup> 303.1380, found 303.1382.

**2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)cyclopentanone** (**3ia**): Dark brown soild, diastereomeric ratio 6.92:1, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 7.29-7.15 (m, 4H), 7.11-7.07 (m, 1H), 7.02 (d, J= 8. Hz, 2H), 6.92 (d, J= 7.6 Hz, 1H), 6.77 (t, J= 7.64 Hz, 1H), 5.58 (s, 1H), 3.57-3.46 (m, 2H), 3.04-2.89 (m, 2H), 2.74-2.69 (m, 1H), 2.30-2.23 (m, 1H), 2.08-2.02 (m, 2H), 1.85-1.75 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 202.9, 153.4, 153.1, 143.7, 134.6, 129.9, 129.3, 129.0, 128.3, 128.1, 127.8, 125.3, 123.4, 123.0, 116.52, 116.48, 48.5, 42.7, 32.0, 31.0, 29.8, 21.6, 14.6; HRMS (EI) m/z calcd for C<sub>20</sub>H<sub>21</sub>NNaO [M+Na]<sup>+</sup> 314.1462, found 314.1451.

**2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)cyclohexanone** (**3ib**): Yellow oil, diastereomeric ratio = 1.3:1; isolated major isomer, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.23 (dd, J = 12.8, 7.1 Hz, 3H), 7.19 – 7.10 (m, 4H), 6.93 (d, J = 8.1 Hz, 2H), 5.63 (d, J = 4.5 Hz, 1H), 3.82 – 3.67 (m,1H), 3.64 – 3.47 (m, 2H), 2.93 – 2.85 (m, 2H), 2.47 (t, J = 9.9 Hz, 2H), 2.30 (ddd, J = 25.7, 15.3, 9.7 Hz, 2H), 1.86 (d, J = 6.3 Hz, 2H), 1.68 – 1.59 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 214.5, 149.3, 140.3, 135.9, 134.6, 129.3, 128.7, 127.9, 125.8, 118.1, 116.4, 114.9, 112.3, 59.3, 56.5, 54.9, 54.0, 42.6, 41.4, 32.8, 30.2, 28.7, 27.7, 27.0, 25.7, 23.8; HRMS (EI) m/z calcd for C<sub>21</sub>H<sub>23</sub>NNaO<sub>2</sub> [M+Na]<sup>+</sup> 328.1680, found 267.1676.

**2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)cycloheptanone** (**3ic**): Light brown solid, diastereomeric ratio 1:1, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 7.21 (d, J= 8.36 Hz, 1H), 7.20 (d, J = 9.16 Hz, 1 H), 7.11-7.02 (m, 4H), 6.90 (d, J= 8.4 Hz, 2H), 6.68 (t, J= 7.64 Hz, 1H), 5.41 (d, J= 8.4, 1H), 3.55 (t, J= 6.12 Hz, 2H), 3.06-2.97 (m, 2H), 2.87-2.80 (m, 1H), 2.43-2.35 (m, 1H), 2.25-2.19 (m, 1H), 2.11-2.06 (m, 1H), 1.87-1.78 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 215.4, 149.8, 138.7, 134.3, 129.2, 128.3, 127.1, 126.7, 126.2, 117.0, 113.3, 70.3, 65.1, 63.4, 59.5, 57.9, 44.3, 43.0, 31.9, 29.6, 29.4, 29.0, 28.2, 27.2, 24.8, 23.5, 22.6, 14.0; HR-MS (ESI positive) m/z: calcd. for C<sub>22</sub>H<sub>25</sub>NNaO [M+Na]+: 342.181672; found: 342.181517.

**1-phenyl-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)ethanone** (3ja): Yellow solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.84 (d, J = 7.0 Hz, 2H), 7.53 (t, J = 7.7 Hz, 1H), 7.41 (t, J = 7.5 Hz, 2H), 7.25 (t, J = 7.0 Hz, 3H), 7.14-7.10 (m, 3H), 6.96 (d, J = 8 Hz, 2H), 6.75 (t, J = 7.2 Hz, 1H), 5.67 (t, J = 5.4 Hz, 1H), 3.64-3.54 (m, 3H), 3.41 (dd, J = 16.7, 7.0 Hz, 1H), 3.13-3.07 (m, 1H), 2.93 (d, J = 16.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 198.6, 148.7, 138.5, 137.2, 134.5, 133.1, 129.3, 128.5, 128.3, 128.1, 127.1, 126.8, 126.2, 117.9, 114.3, 55.0, 45.3, 42.1, 27.6; HR-MS m/z: calcd for C<sub>23</sub>H<sub>21</sub>NNaO[M+Na]<sup>+</sup>: 350.1515; found: 350.1511.

**1-phenyl-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-1-one** (**3jb**): Light yellow oil, diastereomeric ratio 1:1, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 7.63 (d, J= 7.64 Hz, 2H), 7.41 (t, J=7.64 Hz, 1H), 7.28 (t, J=7.6 Hz, 2H), 7.20 (t, J= 8.4 Hz, 2H), 7.03 (t, J= 6.88 Hz, 2H), 6.99 (d, J= 9.16 Hz, 2H), 6.88 (t, J= 6.88 Hz, 1H), 6.84 (t, J= 7.64 Hz, 1H), 6.68 (t, J= 7.64 Hz, 1H), 5.39 (d, J= 9.16 Hz, 1H), 3.99-3.94 (m, 1H), 3.63-3.59 (m, 2H), 3.05-2.99 (m, 1H), 2.92-2.87 (m, 1H), 1.27 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 204.5, 137.5, 134.4, 132.9, 129.2, 128.1, 127.3, 126.9, 126.0, 113.4, 70.3, 65.2, 63.4, 48.3, 34.2, 31.9, 29.7, 24.9, 22.7, 16.6, 14.1; HR-MS (ESI positive) m/z: calcd. for C<sub>24</sub>H<sub>23</sub>NNaO [M+Na]<sup>+</sup>: 364.168792; found: 364.168681.

#### 2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-1-(p-tolyl)propan-1-one

(**3jc**): Brown solid, diastereomeric ratio 1:1, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 7.44 (d, J= 8.4 Hz, 2H), 7.11-7.07 (m, 3H), 6.98 (d, J=8.4 Hz, 2H), 6.93-6.85 (m, 4H), 6.77 (t, J= 8.4 Hz, 1H), 6.73 (t, J= 6.88 Hz, 1H), 6.56 (t, J= 7.64 Hz, 1H), 5.29 (d, J= 9.16 Hz, 1H), 3.87-3.79 (m, 1H), 3.50 (t, J = 6.08 Hz, 2H), 2.95-2.88 (m, 1H), 2.81-2.74 (m, 1H), 2.18 (s, 3H), 1.13 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm): 205.6, 137.6, 134.6, 133.1, 130.2, 128.1, 127.4, 126.5, 126.3, 114.1, 71.3, 65.2, 63.6, 48.2, 34.3, 31.7, 29.5, 24.7, 22.5, 16.7, 13.3 14.1; HR-MS (ESI positive) m/z: calcd. for C<sub>25</sub>H<sub>25</sub>NNaO [M+Na]<sup>+</sup>: 378.178982; found: 378.178817.

**9-(2,4-dimethoxyphenyl)-9H-xanthene (6a):** White solid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 7.20 (td, J = 8.2 Hz, J = 1.4 Hz, 2H), 7.12-7.08 (m, 4H), 6.97 (td, J = 7.7 Hz, J = 1.3 Hz, 2H), 6.86 (d, J = 8.4 Hz, 1H), 6.48 (s, 1H), 6.35 (dd, J = 1.3 Hz, 2H), 6.86 (d, J = 8.4 Hz, 1H), 6.48 (s, 1H), 6.35 (dd, J = 1.3 Hz, 2H), 6.86 (d, J = 8.4 Hz, 1H), 6.48 (s, 1H), 6.35 (dd, J = 1.3 Hz, 2H), 6.86 (d, J = 8.4 Hz, 1H), 6.48 (s, 1H), 6.35 (dd, J = 1.3 Hz, 2H), 6.86 (d, J = 8.4 Hz, 1H), 6.48 (s, 1H), 6.35 (dd, J = 1.3 Hz, 2H), 6.86 (d, J = 8.4 Hz, 1H), 6.48 (s, 1H), 6.35 (dd, J = 1.3 Hz, 2H), 6.86 (d, J = 8.4 Hz, 1H), 6.48 (s, 1H), 6.35 (dd, J = 1.3 Hz, 2H), 6.86 (d, J = 8.4 Hz, 1H), 6.48 (s, 1H), 6.35 (dd, J = 1.3 Hz, 2H), 6.86 (d, J = 8.4 Hz, 1H), 6.48 (s, 1H), 6.35 (dd, J = 1.3 Hz, 2H), 6.86 (d, J = 8.4 Hz, 1H), 6.48 (s, 1H), 6.35 (dd, J = 1.3 Hz, 2H), 6.86 (d, J = 1.3 Hz, 1H), 6.48 (s, 1H), 6.35 (dd, J = 1.3 Hz, 2H), 6.86 (d, J = 1.3 Hz, 1H), 6.48 (s, 1H), 6.35 (dd, J = 1.3 Hz, 2H), 6.86 (d, J = 1.3 Hz, 1H), 6.48 (s, 1H), 6.35 (dd, J = 1.3 Hz, 2H), 6.86 (d, J = 1.3 Hz, 1H), 6.48 (s, 1H), 6.35 (dd, J = 1.3 Hz, 2H), 6.86 (d, J = 1.3 Hz, 1H), 6.48 (s, 1H), 6.35 (dd, J = 1.3 Hz, 1H), 6.48 (s, 1H

8.4 Hz, J = 2.4 Hz, 1H ), 5.72 (s, 1H), 3.84 (s, 3H), 3.75(s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm): 159.3, 157.1, 151.5, 130.7, 129.3, 128.1, 127.6, 125.1, 123.0, 116.2, 104.8, 98.7, 55.6, 55.2, 36.4; HRMS: calcd for C<sub>21</sub>H<sub>18</sub>NaO<sub>3</sub> [M+Na]<sup>+</sup> 341.1153, found: 341.1141.

**9-(2,4-dimethoxyphenyl)-4-methoxy-9H-xanthene** (6b): White solid, diastereomeric ratio 1:1.3, <sup>1</sup>H NMR (400 MHz)  $\delta$  (ppm): 7.20 (d, J= 8.4 Hz, 1H), 7.13 (dt, J=8.4 Hz, 1H), 7.08 (d, J= 7.64 Hz, 1H), 6.91 (dt, J= 7.6 Hz, 1H), 6.85 (t, J= 7.64 Hz, 1H), 6.82 (d, J= 8.4 Hz, 1H), 6.75 (d, J= 7.64 Hz, 1H), 6.70 (d, J= 7.64 Hz, 1H), 6.43 (s, 1H), 6.32 (dd, J= 8.4 Hz, 1H), 5.69 (s, 1H), 3.91 (s, 3H), 3.80 (s, 3H), 3.70 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 160.3, 159.7, 159.3, 158.4, 157.0, 151.2, 149.6, 147.7, 141.0, 137.5, 132.9, 130.6, 130.1, 129.5, 129.3, 128.4, 128.0, 127.3, 126.6, 126.5, 126.4. 126.3, 125.9, 124.9, 123.2, 122.5, 122.2, 121.1, 119.6, 116.5, 116.1, 110.3, 109.7, 104.8, 104.0, 103.7, 100.2, 98.8, 98.7, 59.5, 56.2, 55.2, 45.6, 36.2, 31.9, 29.6, 22.6, 14.1; C<sub>22</sub>H<sub>20</sub>NaO<sub>3</sub> [M+Na]<sup>+</sup> 371.1288, found: 317.1280.

**9-(2,4-dimethoxyphenyl)-9H-thioxanthene (6c):** Light yellow solid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 7.39-7.34 (m, 4H), 7.16-7.14 (m, 4H), 6.98 (d, *J* = 8.28 Hz, 1H), 6.46 (s, 1H), 6.34 (d, *J* = 8.5 Hz, 1H), 5.64 (s, 1H), 3.84 (s, 3H), 3.73(s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm): 159.7, 157.5, 137.6, 133.0, 130.2, 130.1, 129.9, 129.6, 126.9, 126.7, 126.5, 126.4, 126.0, 124.6, 122.3, 106.2, 104.0, 98.8, 55.3, 45.7, 29.8. HRMS: calcd for C<sub>21</sub>H<sub>18</sub>O<sub>2</sub>S [M+Na]<sup>+</sup> 357.0972, found: 357.0969.

**4-methyl-3-(9H-xanthen-9-yl)phenol (6d):** Light yellow solid, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm):11.71(s,1H), 7.48-7.35 (m, 4H), 7.19-7.04 (m, 3H), 7.02-6.97 (m, 2H),6.89-6.84 (m, 1H), 6.73(dd, *J*= 6.6Hz , *J*=2.0 Hz, 1H), 5.28 (s, 1H), 4.90 (s, 1H), 2.24 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm): 161.8, 155.8, 149.0, 142.6, 138.7, 133.3, 132.5, 130.1, 128.3, 126.5, 122.7, 122.3, 120.0, 119.2, 118.5, 117.7, 117.3, 115.1, 29.8, 20.5. HRMS: calcd for C<sub>20</sub>H<sub>16</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> 311.1067, found: 311.1064.

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## Appendix-Chapter 3

# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of C-C coupling product













Chapter 3


























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Photo Enhancement Decomposition of TBHP: A Convenient and Greener Pathway for Aqueous Domino synthesis of Quinazolinones and Quinoxalines

#### **4.1 Introduction**

The quinazolinone and quinoxaline cores are privileged nitrogenous heterocycles owing to their existence in a variety of bioactive natural products (Scheme 4.1) and play a significant role in medicinal chemistry as anticancer agents, antiinflammatory agents, antibacterial agents and anticonvulsant piriqualone.<sup>[1-5]</sup> In addition, some of the quinazolinones are known to have therapeutic values in the treatment of tuberculosis. Consequently, development of sustainable, costeffective and more efficient methods for the preparation of these heterocycles is of continuous interest. The classical method of quinazolinones synthesis involves condensation of aldehydes and 2-aminobenzamides resulting in aminal intermediates followed by their oxidation to quinazolinones. However, use of chemically unstable aldehydes as starting materials and hazardous oxidants such as KMnO<sub>4</sub>, CuCl, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) etc. brings significant limitations in this method.<sup>[6-7]</sup> Among several synthetic strategies developed so far, a direct oxidative cyclization leading to N-heterocyclic rings has received significant importance due to wide availability of the starting materials, anthranilamides and alcohols.<sup>[8]</sup> However, a catalytic approach is necessary for achieving high activity and selectivity as the reaction involves dehydrogenation of both C-H and N-H bonds in a one-pot procedure. Various transition metal complexes such as Ir, Pd, Cu etc. show efficient activity for the synthesis of these heterocycles, however most of the reactions are performed either at elevated temperature or using organic solvents.<sup>[9-14]</sup> Considering the great emphasis on the green and sustainable chemistry, development of environmental friendly catalytic processes using water as a non-toxic and



Scheme 4.1: Biological active quinazolinones.

abundant solvent is one of the prime challenges. Recently Kundu *et. al.* reported the synthesis of N-heterocyclic moieties using Ir complexes in water medium under reflux conditions.<sup>[15]</sup> On the other hand, free radical chemistry is a powerful tool in the construction of useful reactive intermediates under mild reaction conditions and various synthetic strategies have been adopted for the generation of free radicals and using these radical intermediates in organic synthesis. TBHP is a cost effective and widely used oxidant and radical initiator. TBHP is relatively stable as compared to H<sub>2</sub>O<sub>2</sub> towards thermal decomposition and has been certified for truck shipment in many countries.<sup>[16]</sup> Various heterogeneous catalysts such as ZnI<sub>2</sub>,  $\alpha$ -MnO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>-CND etc. show efficient catalytic activity for the quinazolinone synthesis when coupled with TBHP as oxidant.<sup>[17-18]</sup>

In second chapter, we have reported carboxyl functionalized carbon dots (c-CD) coupled with TBHP as an oxidant for oxidation of chemically inert benzylic C-H bond to their corresponding ketonic form under visible light irradiation. This result encouraged us to investigate the activity of this c-CD and TBHP catalytic system for the cross dehydrogenative coupling reaction such as cyclo-oxidative domino synthesis of N-heterocyclic quinazolinones and quinoxaline derivative. Interestingly, in our initial optimization studies we found that under visible light irradiation, TBHP alone gave higher product yield compared to the c-CD-TBHP system. This result diverted our perception and motivated us to explore the mystery behind the observation.

The catalytic efficiency of TBHP mediated reactions largely depend on the rate of TBHP decomposition into its radicals induced by the supporting metal based catalytic systems. TBHP is well-known to form free-radicals (t-BuO<sup>-</sup>) at elevated temperature through the homolysis of the weak O-O (peroxo) bond, which is potentially used for the oxidation of benzylic alcohol and C-H bond oxidation.<sup>[19-20]</sup> We assumed that *t*-BuO<sup>-</sup> free radicals can be generated through the homolysis of O-O bonds under visible light.

Satisfyingly our strategy worked well, which could be harnessed for the synthesis of quinazolinones from benzyl alcohol as a starting material through a one-pot cascade reaction. The involvement of  $\alpha$ -hydroxyalkyl or alkoxy radical intermediates led to the formation of aldehydes which undergoes cyclization in

presence of benzylamides to yield the final products, thus providing a catalyst free, simple strategy to obtain these biologically important moieties in water under mild reaction conditions.



Scheme 4.2: Reactive oxy free radical generated from TBHP.

#### **4.2 RESULTS AND DISCUSSION**

#### 4.2.1 Optimization studies and substrate scope

The initial assessment of the reaction between benzyl alcohol and anthranilamide were carried out as a model reaction with carboxyl group rich carbon dots (c-CDs) in presence of TBHP (47 % Entry 1 Table 4.1) as an external oxidant under visible light irradiation. However the contradiction arose, when we performed the reaction with TBHP in absence of c-CDs catalyst. It was found that in absence of c-CDs catalyst, the product yield of reaction increases up to 63% with TBHP (2 equiv.) and to 89% with 3.2 equivalent of TBHP, keeping all the other conditions similar (Entries 2 and 3 Table 4.1) at room temperature under visible light irradiation. Although we don't have any evidential explanation for such detrimental effect of c-CDs on the reaction, however it might be attributed to the passivation of the photo- catalytically active surface traps on the c-CD surface by  $-NH_2$  group of anthranilamide or c-dots itself engaged as electron acceptor-donor pair with the substrate molecules. Another possibility for the poor product yield might be the deactivation of the free radicals generated from the TBHP decomposition as c-dots can act as radical scavenger as well.<sup>[21-22]</sup>

Further increase in TBHP amount, resulted no appreciable increase of product yield (Entry 4 Table 1). The results were pleasantly surprising as use of other commercially available oxidants such as H<sub>2</sub>O<sub>2</sub>, di-tert-butyl hydroperoxide (DTBP) or urea peroxide did not result in satisfactory yield of the desired product under similar reaction conditions (Entries 6-8, Table 4.1). In order to compare the photolytic behaviour of TBHP with thermolysis, we performed the model reaction at 90 °C in the presence of 3.2 equivalents of TBHP in the absence of visible light irradiation, which resulted in only 36% of the desired product (Entry 5, Table 4.1). The results suggest that visible light played a critical role in TBHP activation for the cyclo-oxidative reaction. Among all the solvents screened, performing the reaction in water as the solvent afforded the best yield of the quinazolinone. Performing the reaction under N<sub>2</sub> environment did not have a significant impact on the product yield (Entry 9, Table 1). Additionally, in order to confirm the role of visible light on the reaction, the progress of the reaction was monitored by turning off the visible light source from time to time. Negligible progress in the formation of the C-N coupling product was observed without the visible light irradiation (Figure 4.1).



*Figure 4.1:* Progress of the photooxidative coupling reaction of benzyl alcohol and 2aminobenzamide under visible light irradiation (pink) and in dark condition (green) under the optimized reaction conditions. The lamp was turned off from time to time, and the formation of the desired product quinazoline was monitored using a GC instrument.

Having the optimized reaction conditions in hand, we evaluated the substrate scope for the reaction. A wide range of quinazolinones could be synthesized using various primary alcohols as substrates that react with 2-aminobenzamide to afford good to excellent yields in presence of TBHP under visible light irradiation. Both electron withdrawing and donating substituents (NO<sub>2</sub>, -CH<sub>3</sub>, and -OCH<sub>3</sub>) in the phenyl ring of alcohol could be inserted into quinazolinone skeleton with significant yield (entry 3ae, 3af and 3ag, table 2).

#### Table 4.1: Optimization of reaction conditions<sup>a</sup>

ОН +			O NH	
1a	2a	Solvent	3aa	

Entry	Catalyst	Oxidant	Solvent	<sup>b</sup> Yield (%)	Sel (%)
<sup>c</sup> 1	c-CDs	TBHP (2eq)	H <sub>2</sub> O	47	72
2		TBHP (2 eq)	$H_2O$	63	86
3		<b>TBHP (3.2 eq)</b>	$H_2O$	89	97
4		TBHP (5 eq)	$H_2O$	92	98
<sup><i>d</i></sup> 5		TBHP (3.2 eq)	$H_2O$	36	95
6		H <sub>2</sub> O <sub>2</sub> (3.2 eq)	$H_2O$	32	53
7		DTBP (3.2 eq)	$H_2O$	Trace	
8		Urea peroxide	$H_2O$	Trace	
		(3.2eq)			
<sup>e</sup> 9		TBHP (3.2 eq)	$H_2O$	83	91
10		TBHP (3.2 eq)	Toluene	53	93
11		TBHP (3.2 eq)	MeOH	26	87
12		TBHP (3.2 eq)	DMSO	23	91

<sup>*a*</sup>Unless otherwise specified, all the reactions were carried out with benzyl alcohol (2 mmol, 208  $\mu$ L) and 2-aminobenzamide (1 mmol, 136 mg) as the model substrates; illuminated under a 40 W white LED lamp for 14h at 25 °C, <sup>*b*</sup>isolated yield, <sup>*c*</sup>in presence of c-CDs (15mg), <sup>*d*</sup>under dark condition at 90 °C, <sup>*e*</sup>under N<sub>2</sub> environment.

Halogen-substituted benzyl alcohols could be coupled effectively to form the corresponding quinazolinones with good yield under the optimized reaction conditions (entry 3ab, 3af and 3ag, table 2). The olefinic C=C bond of cinnamyl alcohol is also well persisted under the reaction conditions and resulted in corresponding quinazolinone with 79% yield (entry 3ah, table 2). 5-chloro-2aminobenzamide was also found to be compatible under the present reaction





<sup>a</sup>Unless otherwise specified, all the reactions were carried out with alcohol (2mmol) and 2aminobenzamide (1 mmol) in presence of 70% aqueous TBHP (3.2 equivalents, 3.2 mmol = 440  $\mu$ L)illuminated under a 40 W white LED lamp 12h at 25 °C.

conditions and yielded the desired products with excellent yields (entry 3ba, 3bb, 3bc, 3bd and 3be, table 2). Heteroatom containing primary alcohols such as 2pyridine methanol, furfuryl alcohol and 2-thiophene methanol also could be coupled effectively with both 2-aminobenzamide and 5-chloro-2aminobenzamide under the optimized reaction condition with their corresponding products in high yield (entry 3ai, 3aj, 3ak, 3be, 3bf and 3bg table 2). Aliphatic alcohols were not suitable as substrates under the present reaction conditions, as we obtained negligible yield of the desired coupling products. The present methodology is also suitable for large-scale synthesis as we could obtain high yield of quinazolinone in the presence of TBHP under visible light irradiation (75 % yield, Scheme 3) for the model coupling reaction of benzyl alcohol and 2aminobenzamide.



Scheme 4.3: Gram scale synthesis of 2-phenylquinazolin-4(3H)-one.

#### 4.2.2 Mechanistic Investigation

From the studies, it could be clearly ascertained that the formation of free radicals through the decomposition of TBHP was greatly influenced by visible light irradiation as no other photocatalyst was present in the medium. To confirm the hypothesis, we performed a fluorescence based experiment where the free radical generation from TBHP under visible light irradiation was studied using terephthalic acid as the probe molecule. It is well-known that terephthalic acid preferentially reacts with 'OH radicals to form a highly fluorescent product (i.e. 2-hydroxy terephthalic acid) (Figure 4.2).<sup>[23]</sup>Terephthalic acid itself is weakly fluorescent, however upon irradiation of visible light with TBHP, the

fluorescence intensity dramatically increased at 425 nm that enhanced with time. The result suggests that under visible light irradiation, the decomposition of TBHP resulted in the formation of 'OH radicals and consequently the fluorescent 2-hydroxy terephthalic acid formation also increases. Under the thermal condition (90 °C) also, there was a significant enhancement in the fluorescent intensity, however, it was quite lower as compared to the visible light irradiation. The result suggests that the decomposition rate of TBHP is significantly higher under visible light than at elevated temperature resulting in faster free radical generation.



**Figure 4.2:** (a) Formation of fluorescent 2-hydroxy terephthalic acid by hydroxyl radical; (b) Fluorescence spectra of an aqueous solution of terephthalic acid and TBHP under visible light and thermal conditions (90 °C) showing the emission of 2-hydroxy terephthalic acid; (c) Time-dependent fluorescence changes at 425 nm due to the oxidation of terephthalic acid by TBHP under visible light irradiation and under thermal condition (90 °C).

A few controlled experiments were performed to understand the participation of various free radicals in the reaction. The reaction was significantly inhibited in the presence of a radical scavenger, butylated hydroxytoluene (BHT). The result clearly confirms the involvement of free radicals in the reaction mechanism. On the other hand, addition of a 'OH radical scavenger, tert-butyl alcohol (TBA) in the reaction medium, had no effect on the conversion. Similarly, addition of *p*-benzoquinone (BQ) as an 'O<sub>2</sub><sup>-</sup> scavenger has no impact in the reaction (Figure 4.3). From these studies, it could be inferred

that 'OH or ' $O_2^-$  radicals were not involved in the reaction mechanism and probably alkoxy free radicals were responsible in the oxidation of alcohols to aldehydes, which was formed as an intermediate.

A few control experiments were further carried out to gain insight into the reaction mechanism (Scheme 4.4). Whereas, the visible light mediated reaction of benzaldehyde and 2 aminobenzamide in the presence of TBHP as the oxidant yielded quinazolinone as the exclusive product, only dihydroquinazolinone was obtained as the major product in absence of TBHP. Therefore, it can be concluded



*Figure 4.3: a)* Control experiments demonstrating the effect of various free radical scavengers on *the visible light mediated quinazolinone synthesis: butylatedhydroxytoluene (BHT), p-benzoquinone (BQ, 'O\_2' scavenger), tert-butyl alcohol (TBA, 'OH radical scavenger).* 

that benzaldehyde and dihydroquinazolinone could be the intermediates in the model coupling reaction of benzyl alcohol and 2 aminobenzamide. TBHP not only acted as an oxidant for the conversion of alcohol to aldehyde but also participated in the oxidation of dihydroquinazolinone to yield the final products. The reaction rate during the oxidation of dihydroquinazolinone was not affected by the presence of a radical scavenger such as BHT, thus eliminating the involvement of any radical process. Similarly, p-benzoquinone (BQ) as an  $O_2^-$  scavenger has no impact in the reaction. The results suggest that the oxidation of the O-H bonds in the present system could not be associated with 'OH or  $O_2^-$  radicals.

Based on the control experiments, a probable reaction sequence for

quinazolinone synthesis is shown in scheme 4.5. In the first step, which is the rate-determining step, oxidation of benzyl alcohol to their corresponding aldehyde takes place through the involvement of visible light induced *tert*-BuO<sup>·</sup> radicals generated from TBHP. The *tert*-BuO<sup>·</sup> radical abstracts a hydrogen from benzyl alcohol to give the  $\alpha$ hydroxybenzyl radicals. Due to the polar effect, the hydroxybenzyl radicals undergo a classic alkoxy radical disproportionation reaction between *tert*-BuO<sup>·</sup> radical and carbon atom to generate benzaldehyde. Benzaldehyde then reacts with 2-aminobenzamide and undergo intra-molecular cyclization to generate dihydroquinazolinone. Finally, oxidation of dihydroquinazolinone by TBHP results in the final product quinazolinone.



*Scheme 4.4:* Control experiments with benzaldehyde and 2-aminobenzamide as the starting materials.



Scheme 4.5: Proposed mechanism for quinazolinone synthesis upon visible light irradiation.

The methodology could be further extended towards the synthesis of another important class of bioactive moieties, quinoxalines, through the sequential oxidation of aryl substituted  $\alpha$ -hydroxy ketones followed by condensation with aryl 1,2-diamine using TBHP as the oxidant under visible light irradiation in water. Both electron withdrawing and electron donating substituents on the aromatic ring afforded the corresponding quinoxaline product with good yield (79% to 93% Table 4.3). Further, heterocyclic furan and thiophene groups could be introduced in the moiety under the visible light irradiation with excellent product yield (87% and 90% respectively Table 4.3, 6a-6h).

Table 4.3: Visible light mediated synthesis of quinoxaline in presence of TBHP



<sup>*a*</sup>Unless otherwise specified, all the reactions were carried out with  $\alpha$ -hydroxyl ketone (1mmol) and diamine (1 mmol) in presence of 70% aqueous TBHP (3.2 equivalents, 3.2 mmol = 440  $\mu$ L

)illuminated under a 40 W white LED lamp 8h at 25 °C.

## 4.3 Conclusion

In summary, TBHP decomposes faster when irradiated with visible light to generate free radicals. This phenomenon can be successfully applied for a straightforward synthesis of N-heterocyclic moieties such as quinazolinone and quinoxaline in water using alcohols as the starting materials under mild reaction conditions. This protocol that involves no metal or external photocatalysts can be utilized for green synthesis of important bioactive molecules through radical chemistry.

## 4.4 Experimental Section

#### 4.4.1 Materials

*Tert*-butylhydroperoxide (TBHP), hydrogen peroxide and all other chemicals were purchased from Sigma-Aldrich, India or Merck, India and used without further purification. We used Millipore water (ultrapure level) throughout the experiments.

#### 4.4.2 Photomediated synthesis of quinazolinone

In a typical reaction, 2.0 mmol of the alcohol substrate, 0.75 mmol of the anthranilamide, 3 equivalent of TBHP and 4 mL of  $H_2O$  were taken in a reaction vial and the mixture was exposed to visible light using a 40 Watt white LED lamp for 12 h, using a home-made photoreactor system. Magnetic stirring was performed throughout the reaction. The temperature of the reaction was maintained at 28 °C. The progress of the reaction was monitored by TLC using ethyl acetate and hexane as eluent. After completion of the reaction, the resulting mixture was extracted with ethyl acetate (3 x 20 ml) and washed with water (1 x 15 ml). The organic layer was dried over anhydrous sodium sulphate and evaporated under reduced pressure to get the residue. The residue was purified using silica gel column chromatography (100-200 mesh) where a mixture of hexane and ethyl acetate was used as eluent.

#### 4.4.3 Photomediated synthesis of quinoxalines

For the quinoxaline synthesis, 1.0 mmol (226 mg) of  $\alpha$ -hydroxy ketone, 1.0 mmol of diamine (108 mg) and 3.2 equivalents of 70% aqueous TBHP (440

 $\mu$ L) was taken in a vial containing 4 mL of water and was subjected to visible light illumination from a 40 watt LED lamp for 8 h. The progress of the reaction was monitored by TLC using ethyl acetate and hexane as eluent. After completion of the reaction, the resulting mixture was extracted with ethyl acetate (3 x 20 ml) and washed with water (1 x 15 ml). The organic layer was dried over anhydrous sodium sulphate and evaporated under reduced pressure to get the residue. The residue was purified using silica gel column chromatography (100-200 mesh) where a mixture of hexane and ethyl acetate was used as eluent.

#### 4.4.4 Optimized Tert-butylhydroperoxide (TBHP) concentration



The overall reaction for the synthesis of quinazolinone is represented as:

If we consider the reaction in stepwise manner, there are two oxidation steps which require TBHP as an external oxidant.



From above, it is evident that for the first oxidation step, i.e oxidation of 2 mmol benzyl alcohol to benzaldehyde, it requires at least 2 mmol of TBHP. And for the 2nd oxidation step, i.e oxidation of 1 mmol dihydroquinazolinone (assuming that all 1 mmol of limiting reagent 2-aminobenzamide gets converted in the dihydroquinzolinone) to quinazolinone, it again requires 1 mmol of TBHP, so the minimum amount of TBHP required for complete conversion will be 3 mmol, i.e 3 equivalents of TBHP.

Considering the concentration of 1.0 mmol of the limiting reagent (2aminobenzamide), used in the reaction, a minimum of 3.0 mmol of TBHP is required for complete conversion. We used 3.2 equivalent (3.2 mmol) of TBHP for the reactions as the optimal concentration, which is a little excess than the stoichiometric concentration.

#### 4.4.5 Characterization Data

# 4.4.5.1 Characterization Data of synthesized quinazolione and quinoxaline product

**2-phenylquinazolin-4(3***H***)-one (3aa):** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 11.30$  (br, s, 1H), 8.35-8.33 (d, *J*=7.68, 1H), 8.24-8.22 (m, 2H), 7.86-7.79 (m, 2H), 7.60-7.59 (m, 3H), 7.53-7.50 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 163.7$ , 151.7, 149.9, 134.9, 132.9, 131.7, 129.1, 128.0, 127.3, 126.8, 126.4, 120.9.

**2-(4-chlorophenyl)quinazolin-4(3***H***)-one (3ab):** <sup>1</sup>H NMR (DMSO-d<sup>6</sup>, 400 MHz):  $\delta = 12.61$  (br, s, 1H), 8.21-8.19 (d, *J*=8.48 Hz, 2H), 8.17-8.15 (d, *J*=7.72 Hz, 1H), 7.87-7.83 (t, *J*=7.64 Hz, 1H), 7.76-7.74 (d, *J*=8.08 Hz, 1H), 7.64-7.62 (d, *J*=8.4 Hz, 2H), 7.56-7.52 (t, *J*=7.44 Hz, 1H); <sup>13</sup>C NMR (DMSO-d<sup>6</sup>, 100 MHz):  $\delta = 162.6$ , 151.9, 148.9, 136.8, 136.5 135.1, 132.0, 130.0, 129.2, 128.0, 127.3, 126.3, 121.5.

**2-(4-bromophenyl)quinazolin-4(3***H***)-one (3ac):** <sup>1</sup>H NMR (DMSO-d<sup>6</sup>, 400 MHz):  $\delta = 12.63$  (br, s, 1H), 8.19-8.14 (m, 3H), 7.89-7.85 (t, J = 7.04 Hz, 1H), 7.80-7.76 (m, 3H), 7.58-7.54 (t, J = 7.6 Hz, 1H); <sup>13</sup>C NMR (DMSO-d<sup>6</sup>, 100 MHz):  $\delta = 162.1$ , 151.9, 135.7, 135.2, 134.4 132.4, 132.1, 130.3, 128.2, 127.4, 126.2, 125.9, 125.7, 121.5.

**2-(4-fluorophenyl)quinazolin-4(3H)-one (3ad):** <sup>1</sup>H NMR (DMSO-d<sup>6</sup>, 400 MHz):  $\delta = 12.59$  (br, s, 1H), 8.20-8.15 (m, 3H), 7.88-7.82 (t, J = 7.04 Hz, 1H), 7.81-7.78 (m, 3H), 7.60-7.56 (t, J = 7.6 Hz, 1H); <sup>13</sup>C NMR (DMSO-d<sup>6</sup>, 100 MHz):  $\delta = 162.3$ , 151.7, 135.5, 135.2, 132.5, 132.3, 130.1, 128.1, 127.4, 126.1, 126.0,125.8,121.5.

**2-(2-nitrophenyl)quinazolin-4(3***H***)-one (3ae):** <sup>1</sup>H NMR (DMSO-d6, 400 MHz):  $\delta = 12.83$  (br, s, 1H), 8.23-8.18 (t, J = 8.24 Hz, 2H), 7.94-7.82 (m, J = 7.28 Hz, 4H), 7.67-7.65 (d, J = 8.04 Hz, 1H), 7.60-7.57 (t, J = 7.78 Hz, 1H);<sup>13</sup>C NMR (DMSO-d<sup>6</sup>, 100 MHz):  $\delta = 161.97$ , 152.12, 148.88, 147.88, 135.13, 134.38, 131.99, 131.96, 129.63, 127.82, 127.58, 126.31, 124.98, 121.62. **2-**(*p*-tolyl)quinazolin-4(3*H*)-one (3af): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 11.34$  (br, s, 1H), 8.26-8.25 (d, J = 7.52 Hz, 1H), 8.07-8.05 (d, J = 8.28 Hz, 2H), 7.76-7.72 (m, 2H), 7.44-7.41 (t, J = 7.76 Hz, 1H), 7.32-7.30 (d, J = 8.0 Hz, 2H); 2.45 (s 3H);<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 164.1$ , 151.7, 149.5, 142.2, 135.1, 130.2, 129.9, 129.8, 129.1, 127.9, 127.4, 126.6, 126.4, 120.7, 21.5.

**2-(4-methoxyphenyl)quinazolin-4(3***H***)-one (3ag):** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 10.74$  (br, s, 1H), 8.25-8.23 (d, J = 7.52 Hz, 1H), 8.09-8.07 (d, J = 8.0 Hz, 2H),7.73(m, 2H), 7.41 (m, 1H), 7.01-6.99 (d, J = 8.04 Hz, 2H), 3.84 (s, 3H); <sup>13</sup>C NMR (DMSO-d<sup>6</sup>, 100 MHz):  $\delta = 163.4$ , 152.1, 148.2, 135.9, 134.5, 129.9, 128.7, 127.3, 127.1, 126.5, 121.3.

(*E*)-2-styrylquinazolin-4(3*H*)-one (3ah): <sup>1</sup>H NMR (DMSO-d<sup>6</sup>, 400 MHz):  $\delta = 11.49$  (br, s, 1H), 7.28-7.26 (d, *J*= 7.4 Hz, 1H), 7.13-7.09 (d, *J* = 16.0 Hz, 1H), 6.97-6.95 (t, *J* = 7.08 Hz, 1H), 6.83 (m, 3H), 6.62 (m, 4H), 6.19-6.15 (d, *J* = 16.0 Hz, 1H);<sup>13</sup>C NMR (DMSO-d<sup>6</sup>, 100 MHz):  $\delta = 161.7$ , 159.8, 151.6, 148.9, 138.3, 135.1, 129.7, 129.0, 127.5, 126.1, 125.6, 121.3.

**2-(pyridin-2-yl)quinazolin-4(3H)-one (3ai):** <sup>1</sup>H NMR (DMSO-d<sup>6</sup>, 400 MHz):  $\delta$  = 11.80 (br, s, 1H),8.75-8.73 (m, 1H), 8.46-8.42 (m, 1H), 8.19-8.15 (m, 1H), 8.09-8.03 (m,1H), 7.89-7.76 (m, 2H), 7.67-7.63 (m, 1H), 7.59-7.53 (m, 1H); <sup>13</sup>C NMR (DMSO-d<sup>6</sup>, 100MHz):  $\delta$  = 160.80, 149.9, 149.0, 148.6, 148.4, 138.0, 134.7, 127.7, 127.3, 126.5, 126.1, 122.2, 122.0.

**2-(furan-2-yl)quinazolin-4(3H)-one (3aj):** <sup>1</sup>H NMR (DMSO-d<sup>6</sup>, 400MHz):  $\delta =$  12.49 (br, s, 1H), 8.12-8.10 (d, J = 8.04 Hz, 1H), 7.99 (m, 1H), 7.82-7.78 (t, J = 8.52 Hz, 1H), 7.69-7.67 (d, J = 8.0 Hz, 1H), 7.62-7.61 (d, J = 3.52 Hz, 1H), 7.50-7.46 (t, J = 7.04 Hz, 1H), 6.74-6.73 (m, 1H); <sup>13</sup>C NMR (DMSO-d<sup>6</sup>, 100 MHz):  $\delta =$  161.6, 148.7, 146.6, 146.1, 144.0, 134.7, 127.3, 126.5, 125.9, 121.1, 114.5, 112.5.

**2-(thiophen-2-yl)quinazolin-4(3H)-one (3ak):** <sup>1</sup>H NMR (DMSO-d<sup>6</sup>, 400 MHz):  $\delta = 12.64$  (br, s, 1H), 8.23-8.21 (d, J = 4.76 Hz, 1H), 8.12-8.10 (d, J = 7.8 Hz, 1H), 7.86-7.85 (d, J = 5.76 Hz, 1H), 7.81-7.77 (t, J = 8.52 Hz, 1H), 7.65-7.63 (d, J = 8.0 Hz, 1H), 7.50-7.46 (t, J = 8.04 Hz, 1H), 7.24-7.21 (m, 1H); <sup>13</sup>C NMR (DMSO-d<sup>6</sup>, 100 MHz):  $\delta = 161.8$ , 148.7, 147.8, 137.4, 134.7, 132.2, 129.4, 128.5, 127.0, 126.3, 125.9, 120.9.

**6-chloro-2-phenylquinazolin-4(3H)-one (3ba):** <sup>1</sup>H NMR (DMSO-d<sup>6</sup>, 400 MHz):  $\delta = 12.69$  (br, s, 1H), 8.16-8.14 (m, 2H), 8.07 (s, 1H), 7.86-7.84 (m, 1H),

7.77-7.75 (m, 1H), 7.61-7.54 (m, 3H); <sup>13</sup>C NMR (DMSO-d<sup>6</sup>, 100 MHz):  $\delta$  = 161.5, 149.1, 147.1, 146.0, 143.9, 133.8, 132.6, 131.8, 127.3, 126.5, 125.7, 121.0, 114.4, 112.9.

**6-chloro-2-(p-tolyl)quinazolin-4(3H)-one (3bb):** <sup>1</sup>H NMR (DMSO-d<sup>6</sup>, 400):  $\delta$  =11.40 (br, s, 1H), 8.32-8.30 (d, *J* = 7.52 Hz, 1H), 8.12-8.10 (s, *J* = 8.28 Hz, 1H), 7.82-7.76 (m, 2H), 7.50-7.46 (t, *J* = 7.76 Hz, 1H), 7.37-7.35 (d, *J* = 8.0 Hz, 2H), 2.89 (s, 3H); <sup>13</sup>C NMR (DMSO-d<sup>6</sup>, 100 MHz):  $\delta$  = 164.3, 151.1, 149.4, 142.2, 134.9, 130.4, 129.8, 129.5, 129.1, 127.7, 127.3, 126.7, 126.1, 120.4, 21.1.

**6-chloro-2-(4-methoxyphenyl)quinazolin-4(3H)-one (3bc):** <sup>1</sup>H NMR (DMSOd<sup>6</sup>, 400 MHz):  $\delta$  = 12.59 (br, s, 1H), 8.20-8.18 (d, *J*=8.8 Hz, 2H), 8.09 (s, 1H), 7.90-7.83 (m, 2H), 7.74-7.72 (d, *J*=8.76 Hz, 1H), 3.34 (s,3H); <sup>13</sup>C NMR (DMSOd<sup>6</sup>, 100 MHz):  $\delta$  = 164.9, 151.8, 148.3, 136.1, 134.5, 129.7, 128.8, 127.4, 127.0, 126.2, 121.2.

**6-chloro-2-(4-fluorophenyl)quinazolin-4(3H)-one (3bd):** <sup>1</sup>H NMR (DMSO-d<sup>6</sup>, 400 MHz):  $\delta$  = 11.90 (br, s, 1H), 7.42-7.38 (m, 2H), 7.25 (s, 1H), 7.04-7.02 (dd, *J*=8.72 Hz , *J*=2.36 Hz, 1H), 6.93-6.91 (d, *J*=8.72 Hz, 1H), 6.58-6.54 (t, *J*=8.76 Hz ,2H); <sup>13</sup>C NMR (DMSO-d<sup>6</sup>, 100 MHz):  $\delta$  = 162.4, 152.6, 148.5, 135.9, 134.8, 129.7, 128.5, 127.8, 127.2, 125.4, 121.2.

(E)-6-chloro-2-(4-styrylphenyl)quinazolin-4(3H)-one (3be): <sup>1</sup>H NMR (DMSO-d<sup>6</sup>, 400 MHz):  $\delta$  = 12.51 (br, s, 1H), 8.05-8.04 (s, 1H), 7.99-7.95 (t, *J*=9.8, 1H), 7.85-7.82 (dd, *J* = 8.76 Hz, *J*= 2.48, 1H), 7.72-7.66 (m, 3H), 7.53-7.41 (m, 5H), 7.03-6.99 (d, *J* = 16.0 Hz, 1H); <sup>13</sup>C NMR (DMSO-d<sup>6</sup>, 100 MHz):  $\delta$ = 163.8, 159.6, 151.1, 149.3, 138.6, 135.2, 129.7, 129.3, 127.5, 126.4, 125.5, 121.0.

**6-chloro-2-(pyridin-2-yl) quinazolin-4(3H)-one (3bf):** <sup>1</sup>H NMR CDCl<sub>3</sub>, 400 MHz):  $\delta = 10.99$  (br, s, 1H), 8.66-8.65 (d, J = 4.76 Hz, 1H), 8.55-8.53 (d, J = 8.04.76 Hz 1H), 8.29 (s, 1H), 7.93-7.88 (m,1H), 7.76-7.68 (m, 2H), 7.50-7.46 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100MHz):  $\delta = 160.78$ , 149.7, 149.4, 148.6, 148.3, 138.1, 134.6, 127.5, 127.3, 126.4, 126.0, 122.1, 122.2.

**6-chloro-2-(furan-2-yl)quinazolin-4(3H)-one (3bg):** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 11.12$  (br, s, 1H), 7.95 (s, 1H), 7.75 (d, J = 7.38 Hz, 1H), 7.74 (d, J = 7.26 Hz, 1H), 7.45 (d, J = 7.26 Hz, 1H), 6.52 (t, J = 6.30 Hz, 1H), 7.25 (d, J = 6.30 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 161.0$ , 156.2, 142.2, 141.7, 133.5, 132.9, 132.2, 127.7, 122.2, 109.9, 109.4.

**2,3-diphenylquinoxaline** (6a): <sup>1</sup>H NMR (CDCl<sub>3</sub>,400 MHz):  $\delta = 8.11-8.09$  (m, 2H), 7.11-7.68 (m, 2H), 7.45-7.43 (d, j= 4H), 7.30-7.14 (m, 6H);<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 153.5$ , 141.2, 139.1, 129.9,129.8 129.2, 128.8, 128.3. **2,3-bis(4-methoxyphenyl)quinoxaline (6b):** <sup>1</sup>H NMR (CDCl<sub>3</sub>,400 MHz):  $\delta = 8.13-8.10$  (m, 2H), 7.73-7.71 (m, 2H), 7.50 (d, j=8.56, 4H), 6.88 (d, j= 8.52, 4H),

3.83 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 164.5$ , 159.8, 152.7, 140.7, 132.0,131.4,130.9, 129.2, 128.7, 113.4, 55.0

**2,3-bis(4-fluorophenyl)quinoxaline (6c):** <sup>1</sup>H NMR (CDCl<sub>3</sub>,400 MHz):  $\delta = 8.16$ -8.14 (m, 2H), 7.91-7.77 (m, 2H), 7.52-7.48 (m, 4H), 7.07-7.03 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 164.5$ , 162.0, 152.2, 141.2, 135.1, 131.9, 130.2, 129.2, 115.7, 115.5.

**2,3-di(furan-2-yl)quinoxaline (6d):** <sup>1</sup>H NMR (CDCl<sub>3</sub>,400 MHz):  $\delta = 8.14-8.12$  (m, 2H), 7.77-7.73 (m, 2H), 7.64-7.62 (m, 4H), 6.66 (m,2H), 6.56-6.55 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 151.6$ , 145.4, 142.1, 140.9, 131.3, 129.0, 112.8, 111.

**2,3-di(thiophen-2-yl)quinoxaline (6e):** <sup>1</sup>H NMR (CDCl<sub>3</sub>,400 MHz):  $\delta = 8.08$ -8.05 (m, 2H), 7.73-7.70 (m, 2H), 7.49-7.48 (d, *J*=5.0, 2H), 7.24-7.23 (m, 2H), 7.04-7.02 (t, *J* = 5, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 135.6$ , 134.6, 128.1, 127.8, 126.7, 126.2, 125.9,124.8.

**2,3-di-p-tolylquinoxaline** (**6f**): <sup>1</sup>H NMR (CDCl<sub>3</sub>,400 MHz):  $\delta = 815-8.13$  (m, 2H), 7.74-7.72 (m, 2H), 7.43-7.41 (d, *J*=8.04, 4H), 7.15-7.13 (d, *J*=7.8, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 153.2$ , 140.9, 138.5, 136.1, 129.4, 128.8, 128.7, 21.1.

**6-chloro-2,3-diphenylquinoxaline** (**6g**): <sup>1</sup>H NMR (CDCl<sub>3</sub>,400 MHz):  $\delta = 8.02$ -8.01 (m, 3H), 7.94 (m, 1H), 7.61-7.48 (m, 8H), 7.25-7.22 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 164.9$ , 161.6, 154.4, 152.8, 142.3, 138.9, 138.1, 129.8, 129.6, 129.3, 128.8, 128.3, 120.6, 113.1.

**6-methyl-2,3-diphenylquinoxaline, (6h):** <sup>1</sup>H NMR (CDCl<sub>3</sub>,400 MHz):  $\delta = 8.07$ -8.04 (d, J = 8.52, 1H), 7.94 (m, 1H), 7.61-7.58 (dd, J = 8.8, J = 1.76, 1H), 7.35-7.29 (m, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 153.1$ , 151.3, 141.7, 140.6, 138.8, 131.4, 129.7, 128.1, 127.8, 127.1, 126.8, 126.5.

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Appendix-Chapter 4

<sup>1</sup>H and <sup>13</sup>C NMR Spectra of quinazolinone & quinoxaline products


























Chapter 4











Carbon Dots Supported Iron Oxide Nanoparticles: An Efficient Magnetically Recoverable Visible Light Mediated Photocatalyst for Cross Dehydrogenative Coupling Reactions

#### 5.1 Introduction

Semiconducting photocatalysts such as TiO<sub>2</sub> and ZnO have been extensively used for environmental remediation and chemical synthesis, existing wide band gap in such materials have limited their utilization in visible light mediated catalysis.<sup>[11]</sup> For the efficient utilization of solar light, semiconductor hybrid materials such as iron oxide nanoparticles (NPs) with appropriate band gap, chemical composition, low toxicity and chemical stability has received considerable attention as a promising visible light photocatalyst. However, the photocatalytic efficacy of iron oxide nanoparticles is limited because of some undesirable properties such as particle aggregation and fast recombination of photo excited charge carriers.<sup>[2-4]</sup> In order to improve photocatalytic activity of such narrow band gap semiconductor photocatalysts, various approaches have been developed including functionalization with other semiconducting materials and carbon nanomaterials.<sup>[5-7]</sup>

Similar to the traditional semiconductor quantum dots, CDs can also serve as both electron acceptors or electron donors and allow the electrons transfer between CDs and semiconductor which consequently hinder the electron hole pair recombination rate resulting in enhancement in photocatalytic activity. The oxygen functionalities present on the CDs surface can be exploited for the stabilization of nanoparticle surface to prevent them from agglomeration.<sup>[8-9]</sup> Although photocatalytic activity of CDs/Fe<sub>3</sub>O<sub>4</sub> has been explored for environmental remediation such as dye degradation<sup>[10]</sup> their application for chemical transformations as visible light photocatalyst is still constrained. On account of the presence in natural products tetrahydoisoquinoline (THIQ) derivatives have significant biological applications.<sup>[11]</sup> In recent years various methods have been developed for the synthesis of THIQ derivatives. Among them, CDC coupling of amines, in particular N-Phenyltetrahydroisoquinoline with various nucleophiles has gained significant amount of importance.<sup>[12-13]</sup> Under photocatalytic conditions, two C-H bonds or heteroatom-H bonds can be coupled directly to form a new bond in a process called cross-dehydrogenative coupling (CDC) satisfying the green chemistry criteria of atom economy, [11, 14-18] environmental friendly conditions, molecular oxygen as oxidant, and in most cases water being as the sole by-product.



**Scheme 5.1.** (1). Photocatalytic cross-dehydrogenative coupling of C-H bonds, (2) Photocatalytic cross-dehydrogenative coupling of N-Phenyltetrahydroisoquinoline with nucleophile.

In this chapter, we are reporting CDs stabilized iron oxide NPs as effective magnetically recoverable photocatalyst for cross-dehydrogenative coupling of N-phenyltetrahydroisoquinoline with nucleophiles under visible light irradiation.

#### 5.2 Results and Discussion

# 5.2.1 Synthesis of CDs and CDs stabilized iron oxide nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@CDs)

CDs were first synthesized following a previously reported procedure by microwave treatment of polyethylene glycol-200 (PEG-200).<sup>[19]</sup> In a domestic microwave oven, 50 mL of PEG-200 was subjected to microwave treatment to give a brown suspension which was later purified to give pure CDs by a process called dialysis. These purified CDs were directly used as the stabilizing agent in the synthesis of iron oxide NPs.

Iron oxide NPs were synthesized by the well-known co-precipitation method using FeCl<sub>3</sub> and FeSO<sub>4</sub> salts. The two iron salts were added in a 2:1 ratio to an aqueous solution of CDs. The reaction mixture was vigorously stirred at 60  $^{\circ}$ C under inert atmosphere and 2.5 M NaOH solution was added. The *in situ* synthesized iron oxide NPs were stabilized by the CDs present in the aqueous solution. The unreacted particles were removed by centrifugation and with the help of a magnet. The stabilized NPs were then washed with water and ethanol and dried under vacuum. Citrate-stabilized iron oxide NPs and bare iron oxide NPs were synthesized iron oxide NPs and bare iron oxide NPs were synthesized iron oxide NPs and bare iron oxide NPs were synthesized by a similar co-precipitation method but with Na-citrate

and no stabilizing agent respectively. The synthesized Fe<sub>3</sub>O<sub>4</sub>@CDs NPs were characterized by several spectroscopic and microscopic techniques.

#### 5.2.2 Characterization of Fe<sub>3</sub>O<sub>4</sub>@CDs nanocomposite

Powder X-ray diffraction patterns of Fe<sub>3</sub>O<sub>4</sub>@CDs showed peaks at  $2\theta$  = 30.17, 35.46, 43.38, 53.69, 57.23 and 62.77° correspond to (220), (311), (400), (422), (511) and (440) planes for Fe<sub>3</sub>O<sub>4</sub> NPs were also observed (fig. 5.1 a).<sup>[9]</sup> FTIR studies further revealed the binding of CDs to the iron oxide surface. The area and peak intensity for the oxygenated functional groups such as -C=O and C-O-C (fig. 5.1b) were decreased significantly in the nanocomposite signifying involvement of these functional groups in the stabilization of iron oxide NPs surface. In addition, a peak at 586 cm<sup>-1</sup> for Fe-O stretching in the nanocomposite was also observed.<sup>[20]</sup>

The presence of different functionality and elements in Fe<sub>3</sub>O<sub>4</sub>@CDs was further confirmed by X-ray photoelectron spectroscopy (XPS). The survey spectrum of the composite shows some spectral lines at binding energies (BEs) of about 284.6, 530.7 and 710.7-724.6 eV are attributed to C 1s, O 1s, and Fe 2p, respectively (Fig. 5.1c). Signals appeared at BEs 710.7 and 724.6 eV can be assigned to the Fe2p<sub>3/2</sub> and Fe2p<sub>1/2</sub> levels of Fe<sub>3</sub>O<sub>4</sub> NPs (Fig. 5.1d). The C1s core level spectrum of the composite can be fitted into four components with BEs at about 284.8, 286.2, 287.9 and 289.0 eV which correspond to nonoxygenatedcarbon in C-C, epoxy carbon in C-O, carbonyl carbon in C=O and carboxyl carbon in O-C=O respectively (Fig. 5.2a).<sup>[21-22]</sup> Similarly, O1s core level spectrum of the composite can be fitted into three components with BEs at about 530.7, 532.2 and 533.2 that correspond to anionic oxygen in Fe<sub>3</sub>O<sub>4</sub>, carbonyl oxygen in C=O and alkoxy oxygen in C-O (Fig. 5.2b).<sup>[23]</sup>

Transmission electron microscope (TEM) image showed formation of spherical  $Fe_3O_4$  NPs with average diameter of 7-8 nm (Fig. 5.2c). Presence of a low contrast CD layer ca. 2 nm could be observed in the high resolution TEM image. Selected area electron diffraction confirmed high crystalline nature of the material (Fig. 5.2d).

Further, magnetic susceptibility measurement of Fe<sub>3</sub>O<sub>4</sub>@CDs composite

(Fig. 5.3) showed decrease in magnetization value (48.6 emu/g) of Fe<sub>3</sub>O<sub>4</sub> NPs in the composite compared to that of bare Fe<sub>3</sub>O<sub>4</sub> NPs (64 emu/g).<sup>[9]</sup> Again, this is an indicative of the fact that the Fe<sub>3</sub>O<sub>4</sub> NPs surface has been modified by the presence of CD layer. Moreover, zero coercivity remanence on the magnetization loop, and the absence of a hysteresis loop suggested the super paramagnetic behaviour of Fe<sub>3</sub>O<sub>4</sub>@CDs composite.



**Figure 5.1.** a) Powder X-ray diffraction pattern of  $Fe_3O_4@CDs$  composite, b) FTIR spectra for CDs and  $Fe_3O_4@CDs$  respectively, c) Wide scan XPS spectrum of  $Fe_3O_4@CDs$  and d) Fe2p core level XPS spectrum of  $Fe_3O_4@CDs$ .

## 5.2.3 Photocatalytic activity of Fe<sub>3</sub>O<sub>4</sub>@CDs nanocomposite towards crossdehydrogenative coupling

The catalytic activity of the synthesized catalyst was first investigated by molecular oxygen as the sole oxidant for 12 h in a solvent free condition. This resulted in 88% yield of the desired coupling product (Table 1, entry 1). However, the same reaction performed under conventional heating at 90 °C with no photoirradiation resulted in only 42% yield of the product (Table 1, entry 2). This initial finding showed that the photoirradiation is playing a big part in the observed catalytic activity. On the other hand, bare Fe<sub>3</sub>O<sub>4</sub> NPs showed poor



*Figure 5.2. a) C1s and b) O1s core level XPS spectrum of*  $Fe_3O_4@CDs$ , *c) TEM image of*  $Fe_3O_4@CDs$  with scale bar 20 nm (inset a: high resolution TEM image) and d) SAED pattern.



Figure 5.3. Magnetization curve for CD stabilized iron oxide nanoparticles.

activity for the reaction giving only 40-45% yields irrespective of photoirradiation or conventional heating (Table 5.1, entry 3-4). Again when CDs were used as the catalyst it gave only trace of the product (Table 5.1, entry 5).

These results again showed that  $Fe_3O_4$  or CDs were less effective when used as individual catalysts. The better photocatalytic activity of  $Fe_3O_4$ @CDs could be attributed to the stronger synergistic interaction between CDs and  $Fe_3O_4$  matrix. Further,  $Fe_3O_4$ @CDs was found to be inactive when the reaction was performed by replacing molecular  $O_2$  by air or Ar (Table 5.1, entry 6-7), however similar product yield was obtained when TBHP was used in place of molecular  $O_2$  (Table 5.1, entry 8).Further, citrate stabilized  $Fe_3O_4$  NPs resulted in only 39% yield of the product (Table 1, entry 9). When the reaction was performed in presence of solvents such as DMSO or MeOH, significant decrease in product yield was observed (Table 5.1, entry 10-11). When no catalyst was used keeping other parameters constant, no product formation was observed (Table 5.1, entry 12). After several optimization reactions, the best conditions for the reactions was obtained when performed using 5 wt% of  $Fe_3O_4$ @CDs catalyst under molecular  $O_2$  in a solvent-free medium illuminated under a 40 W white LED lamp.

Table 5.1. Cross-dehydrogenative coupling of 1a and 2a under various conditions<sup>a</sup>

lia	N <sub>Ph</sub> + Me OEt	Photocatal oxidant	vst EtO.	N Ph Me O O 3aa
Entry	Catalyst	solvent	Time	<sup>b</sup> Yield (%)
1	Fe <sub>3</sub> O <sub>4</sub> @CDs (hv)		12	88
<sup>c</sup> 2	$Fe_3O_4@CDs(\Delta)$		12	42
3	$Fe_3O_4$ ( $\Delta$ )		12	40
4	$Fe_3O_4(hv)$		12	45
5	$CD (hv)/(\Delta)$		12	Trace
<sup><i>d</i></sup> 6	Fe <sub>3</sub> O <sub>4</sub> @CDs (hv)		12	Trace
<sup>e</sup> 7	$Fe_3O_4$ @CDs (hv)		12	Trace
<sup>f</sup> 8	Fe <sub>3</sub> O <sub>4</sub> @CDs (hv)		12	83
9	Fe <sub>3</sub> O <sub>4</sub> @citrate		12	39
10	Fe <sub>3</sub> O <sub>4</sub> @CDs (hv)	DMSO	12	35
11	Fe <sub>3</sub> O <sub>4</sub> @CDs (hv)	MeOH	12	26
12			12	

<sup>a</sup>Unless otherwise specified, all the reactions were carried out using N-phenyltetrahydroisoquinoline (0.5 mmol) and ethylacetoacetate (5 mmol) as the model substrates; catalyst (5 mg) illuminated under a 40 W white LED lamp at 25 °C under  $O_2$  environment, <sup>b</sup>isolated yield, <sup>c</sup>Reactions under dark condition at 90 °C, <sup>d</sup> under air, <sup>e</sup>under Ar environment, <sup>f</sup>TBHP.

With the optimized reaction conditions in hand, we evaluated the substrate scope for the reactions. Various nucleophiles have been employed, including active methylene compounds such as nitroalkanes, ketones and electron-rich or electron deficient arenes in N-aryltetrahydroisoquinoline and the results are summarized in table 5.1. N-phenyltetrahydroisoquinoline with different active methylene ketones such as ethylacetoacetate, diethylmalonate, dimethylmalonate gave the corresponding CDC product with excellent yield.

Similarly, nitromethane or nitroethane as nucleophile were also found to be compatible under the reaction conditions and gave the corresponding CDC substituted product with excellent yield. Halo arenes in Naryltetrahydroisoquinoline also reacted well with the nucleophiles and resulted in the corresponding products in 76-90% yield. Electron rich and deficient arenes were also found to be comfortable under the reaction conditions and no obvious decrease in product yield was observed. Reaction of isochroman and nitromethane was also found to be smooth and resulted in corresponding product in 84% yield.





Reaction Conditions: N-aryl-tetrahydroisoquinoline (0.5 mmol) and nucleophile (5 mmol);  $Fe_3O_4@CDs$  (5mg), 40 W white LED lamp at 25 °C, molecular  $O_2$ .

#### 5.2.4 Reaction Mechanism Study

In order to understand the role of CDs in the enhancement of the photocatalytic activity of Fe<sub>3</sub>O<sub>4</sub>@CDs composite, we carried out photoluminescence (PL) and electrochemical impedence spectra measurement (EIS). From the fluorescence studies it was observed that the fluorescence intensity of the CDs was quenched completely in  $Fe_3O_4$ @CDs (Fig. 5.4a). This indicates that there must be some electron transfer involved between CDs and Fe<sub>3</sub>O<sub>4</sub> which consequently protects the Fe<sub>3</sub>O<sub>4</sub> nanoparticles from photocorrosion during photocatalytic process.<sup>[24-25]</sup> The EIS measurement revealed that the charge transfer resistance of Fe<sub>3</sub>O<sub>4</sub>@CDs composite is smaller than that of the pure Fe<sub>3</sub>O<sub>4</sub> (Fig. 5.4b). The ESI results demonstrate that the CDs in Fe<sub>3</sub>O<sub>4</sub>@CDs composites can act as an electron reservoir to trap electrons emitted from Fe<sub>3</sub>O<sub>4</sub> particles. It decreases recombination rate of photoinduced carriers and improves charge transfer.<sup>[26-27]</sup> Again, owing to the upconvesion emission properties, CDs can also excite Fe<sub>3</sub>O<sub>4</sub> nanoparticles to generate electron/hole pairs, consequently the Fe<sub>3</sub>O<sub>4</sub>@CDs can effectively utilize the full spectrum of sunlight to enhancement of the photocataltyic activity.<sup>[28]</sup>



**Figure 5.4.** *a)* Emission spectra for CDs and  $Fe_3O_4$ -CD; b) EIS measurements for  $Fe_3O_4$  (bare) and  $Fe_3O_4@CDs$  composites; c) and d) Band gap of  $Fe_3O_4@CDs$  and  $Fe_3O_4$  (bare) respectively obtained from the UV/Vis spectrum according to the Kubelka–Munk theory.

To further understand the electron transfer process, Kubelka-Munk-transformed reflectance spectrum of pure  $Fe_3O_4$  and  $Fe_3O_4$ @CDs composite was used to evaluate the optical band gap. The calculated band gap of  $Fe_3O_4$ @CDs (2.47 eV) is almost similar to the pure  $Fe_3O_4$  (2.65 eV) within experimental error (fig.5.4 c,d).

In order to have an insight to the possible reaction mechanism we performed a few control reactions. It was observed that the presence of a radical scavenger such as butylated hydroxytoluene (BHT) the product yield of the model coupling reaction was significantly decreased (15%) under optimized conditions. This results suggest that the involvement of free radicals in the reaction pathway. To further specify the reactive species in the photocatalysis process the radical scavenging experiments were carried out which resulted the superoxide radicals ( $O_2^-$ ) are mainly responsible for the photocatalytic transformations (Fig. 5.5).



*Figure 5.5. Free radical scavenging experiment, using a mixture of Phenyltetrahydroisoquinoline and ethyl acetoacetate under optimized conditions.* 

Based on the experimental evidences and literature reports the plausible mechanism for the photocatalytic CDC coupling reaction by  $Fe_3O_4@CDs$  is

shown in the scheme 5.2. At first molecular oxygen (O<sub>2</sub>) and the substrate get O<sub>2</sub> to generate superoxide species.<sup>[29,30]</sup> This superoxide species abstract the  $\alpha$ -C-H bond of **1a** followed by the formation of iminium intermediate which in presence of nucleophiles gives the corresponding desired products with the release of the H<sub>2</sub>O<sub>2</sub> as by-product.



Scheme 5.2: Proposed Mechanism for Photoinduced CDC Reaction of Phenyltetrahydroisoquinoline and ethyl acetoacetate Using  $Fe_3O_4@CDs$  as Photocatalyst in presence of  $O_2$ .

#### 5.2.5 Recovery and reusability study

To ensure the heterogeneity our catalytic system, we performed the model coupling reaction under optimal reaction condition. The reaction was stopped after 50% conversion and the  $Fe_3O_4@CDs$  catalyst were removed from the reaction mixture by centrifugation. The reaction was further continued with the supernatant for 10 h under visible light irradiation; however no further coupling product was formed. The results clearly suggest that the catalytic process is truly heterogeneous in nature (fig. 5.6b). To further determine if any leaching of metal particles occurred during the oxidation reaction, a fraction of the supernatant liquid was analyzed by ICP-AES and the leached metal was found to be 83 ppb (parts per billion), indicating that the leaching was negligible.

Being superparamagnetic in nature, the catalyst Fe<sub>3</sub>O<sub>4</sub>@CDs could be easily recovered from the reaction mixture without having loss in catalyst mass



**Figure 5.6.** *a)* Recovery of the  $Fe_3O_4@CDs$  catalyst with the help of an external magnet, b) study of catalyst reusability for a number of reaction cycles and c) TEM image of  $Fe_3O_4@CDs$  NPs recovered after 5<sup>th</sup> reaction cycle.

with the help of a simple magnet followed by washing with water and ethanol and drying under vacuum (Fig. 5.5a). This recovered catalyst could be used further for multiple iterations (at least up to 5<sup>th</sup> cycle) without no significant loss in catalytic activity maintaining almost 84% of its original activity (Fig 5.5c). However, after 5<sup>th</sup> cycle, catalyst showed gradual decrease in activity which can be attributed to the loss of stabilizing support i.e CDs from the surface of iron oxide NPs which led to agglomeration of the NPs. The XRD pattern also showed structural stability for the catalyst recovered after the 5<sup>th</sup> cycle (fig. 5.5d). This was also evident from the TEM image of catalyst recovered after 5<sup>th</sup> cycle that showed increase in particle diameter (Fig. 5.5e). On the other hand significant loss in catalytic activity was observed for bare and citrate stabilized iron oxide NPs due to loss in structural integrity.

#### **5.3** Conclusion

In conclusion, we have demonstrated carbon dots stabilized iron oxide nanoparticles as a cost-effective, heterogeneous and magnetically recoverable visible light mediated photocatalyst for cross-dehydrogenative coupling of *N*-aryltetrahydroisoquinoline and several nucleophiles. The cooperativity effect between iron oxide NPs and carbon dots was crucial in displaying excellent

photocatalytic activity of the material. It is noteworthy to mentioning that the  $\pi$ - $\pi$  interaction between CDs and the substrates also beneficial to the enrichment of the organic substrates on the surface of the Fe<sub>3</sub>O<sub>4</sub>@CDs composite. Combination of both magnetic behavior as well as photocatalytic activity in the overall material is the focal point of this work which replaces most of the previously reported methodologies. Being environmentally benign in all aspect without compromise in productivity, this methodology can be a great tool for organic synthesis in both academic and industrial research in near future.

#### **5.4 Experimental section**

#### 5.4.1 Materials and methods

PEG-200 used as the source of carbon dots synthesis was purchased from Alfa Aesar. Both iron salts and sodium hydroxide were purchased from Merck India and Rankem respectively. Whereas some of the organic chemicals were synthesized in the laboratory, rest were directly purchased from Sigma aldrich and Merck India and used without further purification. Throughout all manipulations of the work we used Millipore water (ultrapure level).

#### 5.4.2 Synthesis of N-Phenylisoquinoline and its derivatives



In a 250 mL round bottom flask, phenyl boronic acid (3.68 g, 20.0 mmol) and Cu(OAc)<sub>2</sub>.H<sub>2</sub>O (0.2 g, 1.0 mmol) 80 ml CH<sub>2</sub>Cl<sub>2</sub> was taken and stirred for 10 minutes at room temperature. 1,2,3,4- tetrahydroisoquinoline (0.72 g, 0.99 mL, 10.0 mmol) was added to the suspension, and the resulting reaction mixture was stirred at room temperature under an argon atmosphere for 24 h. The progress of the reaction was confirmed by thin layer chromatography. On completion, the crude reaction mixture was subjected to aqueous workup and exctracted with excess of CH<sub>2</sub>Cl<sub>2</sub>. This organic layer was then dried over anhydrous sodiyum sulphate and solvent removed under reduced pressure. The obtained crude

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product was purified by silica gel column chromatography using ethyl acetate and hexane as the eluent (10%-25%). For the derivatives of *N*-Phenylisoquinoline, a similar procedure was followed by choosing the appropriate phenyl boronic acid.



5.4.3 Cross-dehydrogenative coupling of *N*-phenyltetrahydroisoquinoline and ethylacetoacetate



0.5 mmol of *N*-phenyltetrahydroisoquinoline, 5.0 mmol ethylacetoacetate, and 5 mol% of Fe<sub>3</sub>O<sub>4</sub>@CDs catalyst were taken in a glass tube. A balloon filled with molecular oxygen was connected to the tube and the mixture was stirred for 12 h under the photoirradiation of a 40 W white LED lamp at 25 ° C. The progress of the reaction was confirmed by thin layer chromatography. On completion, the reaction was stopped, removed catalyst with the help of a magnet and the reaction mixture was subjected to aqueous work up and extracted with ethyl acetate (3x 20 ml). The combined organic layers were dried over anhydrous sodium sulphate and solvent was removed under rotary evaporator. The crude reaction mixture was column purified using alumina as the stationary phase and 2-5% ethyl acetate/hexane as the eluent.

#### **5.4.4 Characterization data of CDC products**

diethyl 2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate (3b): Yellow oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.84-7.76 (m, 1H), 7.41 (d, *J* = 7.28 Hz, 1H), 7.31-7.27 (m, 2H), 7.20-7.11 (m, 3H), 7.0 (d, *J* = 7.04 Hz, 1H), 6.20-6.14 (m,

1H), 4.15 - 4.10 (m, 2H), 4.05-4.00 (m, 2H), 3.81 - 3.74 (m, 2H), 3.08 (s, 2H), 3.01-2.97 (m, 2H), 1.16-1.11 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  169.5, 166.6, 165.6, 165.0, 141.2, 140.4, 137.0, 132.6, 129.6, 128.9, 126.9 126.1, 125.7, 119.2, 76.4, 75.7, 60.2, 59.4, 50.0, 40.9, 30.2, 28.7, 21.7, 13.3.

#### Dimethyl-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate(3c):

Yellow oil, <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)  $\delta$  7.15 – 7.08 (m, 4H), 7.04 (t, J = 8.04 Hz, 2H), 6.91 (d, J = 8.28 Hz, 2H), 6.69 (t, J = 7.28 Hz, 1H), 5.64 (d, J = 9.28 Hz, 1H), 3.88 (d, J = 9.28 Hz, 1H), 3.66 (s,1H), 3.57 (s,4H), 3.46 (s,3H), 3.02-2.94 (m,1H), 2.82-2.75 (m,1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.3, 167.4, 148.8, 135.7, 134.8, 129.1, 127.7, 127.1, 126.1, 118.7, 115.2, 59.2, 58.2, 52.6, 42.2, 32.0, 31.0, 29.7, 14.2.

**1-(nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline** (**3d**): Yellow oil <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.32-7.14 (m, 5H), 7.02 (d, *J* = 8.04 Hz, 2H), 6.89 (t, *J* = 7.32 Hz, 2H), 5.59 (t, *J* = 7.20 Hz, 1H), 4.91-4.85 (m, 1H), 4.59-4.55 (m, 1H), 3.71 –3.59 (m, 2H), 3.14-3.06 (m, 1H), 2.83-2.77 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  148.8, 135.6, 133.0, 129.7, 129.4, 128.3, 127.2, 126.7, 119.7, 115.2, 58.3, 42.1, 26.4.

**1-(1-nitroethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline** (**3e**): Yellow oil, Isolated diastereomeric ratio = 1.44 : 1; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.20-7.13 (m, mixture of isomers), 7.11-7.02 (m, mixture of isomers), 6.95-6.90 (m, mixture of isomers), 6.77-6.72 (m, mixture of isomers), 5.19-5.15 (m, mixture of isomers), 5.01-4.94 (m, 1H, major isomer), 4.85-4.78 (m, *J* = 8.6, 7.0 Hz, 1H, minor isomer), 3.93-3.91 (m, 1H, minor isomer), 3.80 – 3.73 (m, 1H, major isomer), 3.55-3.45 (m, mixture of isomers), 3.04- 2.94 (m, mixture of isomers), 2.87-2.76 (m, mixture of isomers), 1.63 (d, *J* = 6.8 Hz, 3H, minor isomer), 1.47 (d, *J* = 6.6 Hz, 3H, major isomer); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, mixture of isomers)  $\delta$  149.14 (148.86), 135.60 (134.76), 133.80 (132.01), 129.42 (129.29), 129.09 (128.70), 128.34 (128.19), 127.24 (126.58), 126.12, 119.32 (118.78), 115.41 (114.48), 88.94 (85.43), 62.73 (61.15), 43.55 (42.67), 26.74 (26.39), 17.42 (16.38).

**Dimethyl-2-(2-(3-bromophenyl)-1,2,3,4-tetrahydroisoquinolin-1yl)malonate** (**3f**): Yellow oil, <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 7.26-7.04 (m, 6H), 6.93- 6.86 (m, 2H), 5.68 (d, J = 9.3 Hz, 1H), 3.91 (d, J = 9.4 Hz, 1H), 3.78 (s, 1H), 3.67 (s, 3H), 3.56 (s, 3H), 3.40 (d, J = 10.2, 4.9 Hz, 1H) 3.11-3.04 (m, 1H), 2.97-2.92 (m,1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  167.20, 149.9, 135.60, 134.5, 130.3, 128.90, 127.9, 126.3, 121.2, 117.3, 113.3, 59.0, 57.9, 52.7, 42.4, 29.7, 32.0, 26.3, 14.2.

#### 2-(3-bromophenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline

(3i):Yellow oil <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.24-7.17 (m, 3H), 7.13-7.07 (m, 3H), 6.95-6.87 (m, 2H), 5.52 (t, *J* = 7.28 Hz 1H), 4.86-4.81 (m, 1H), 4.58-4.53 (m, 1H), 3.63 –3.59 (m, 2H), 3.11-3.03 (m, 1H), 2.82-2.76 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  149.6, 135.0, 132.4, 130.7, 129.2, 128.3 , 127.0, 126.8, 123.6, 122.1, 117.6, 113.3, 57.9, 42.0, 29.7, 26.4.

**2-(4-methoxyphenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline** (**3j**): Yellow oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.26-7.13 (m, 4H), 6.93 – 6.81 (m, 4H), , 5.41-537 (t, *J*=6.52 Hz, 1H), 4.85-4.80 (t, *J*=11 Hz,1H), 4.58-4.54 (m, 1H), 3.75 (s, 3H), 3.57 -3.56 (m, 2H), 3.06- 2.98 (m, 1H),2.72-268 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  153.7, 142.7, 135.1, 132.6, 129.1, 127.6, 126.6, 126.3, 118.5, 114.4, 78.6, 58.6, 55.3, 42.8, 31.6, 29.4, 25.5.

**1-(nitromethyl)-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (3k):** Yellow oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.18-7.03 (m, 5H), 6.71 – 6.58 (m, 3H), 5.47-544 (t, *J*= 7.28 Hz,1H), 4.76-4.74 (m, 1H), 3.60 -3.47 (m, 2H), 3.03- 2.95 (m, 1H),2.72-267 (m, 1H),2.24 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  141.2, 130.4, 127.8, 124.8, 124.2, 123.9, 122.8, 121.9, 110.7, 73.7, 58.2, 42.1, 27.0.

**1-(nitromethyl)-2-(4-(trifluoromethyl)phenyl)-1,2,3,4 tetrahydroisoquinoline** (**3l):** Yellow oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.52 (d, *J* = 8.5 Hz, 2H), 7.35-7.02 (m, 6H), , 5.62 (m, 1H), 4.86-4.55 (m, 2H), 3.81 -3.58 (m, 2H), 4.48- 4.44 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  151.2, 135.4, 132.3, 129.3, 128.6, 127.0, 126.8, 126.7, 126.6, 114.3, 77.4, 58.1, 42.0, 26.8.

**4-(nitromethyl)isochroman (3m):** White oil <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.30-7.19 (m, 4H), 4.64-4.62 (m, 2H), 4.59-4.55 (m, 2H), 3.79-3.54 (m, 2H), 3.1-3.07 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  144.6, 135.7, 128.6, 127.5, 125.7, 123.8, 76.8,75.8, 68.0, 35.0.

**1-(nitromethyl)-2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline** (**3l**) : Yellow oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.52 (d, *J* = 8.5 Hz, 2H), 7.35 – 7.02 (m, 6H), , 5.62 (m, 1H), 4.86-4.55 (m, 2H), 3.81 - 3.58 (m, 2H), 4.48- 4.44 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  151.2, 135.4, 132.3, 129.3, 128.6, 127.0, 126.8, 126.7, 126.6, 114.3, 77.4, 58.1, 42.0, 26.8.

**1-(nitromethyl)-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (3k):** Yellow oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.18-7.03 (m, 5H), 6.71 – 6.58 (m, 3H), 5.47-544 (t, *J*= 7.28 Hz,1H), 4.76-4.74 (m, 1H), 3.60 -3.47 (m, 2H), 3.03- 2.95 (m, 1H),2.72-267 (m, 1H),2.24 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  141.2, 130.4, 127.8, 124.8, 124.2, 123.9, 122.8, 121.9, 110.7, 73.7, 58.2, 42.1, 27.0.

**2-(4-methoxyphenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline** (3j): Yellow oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.26-7.13 (m, 4H), 6.93- 6.81 (m, 4H), 5.41-537 (t, *J*=6.52 Hz, 1H), 4.85-4.80 (t, *J*=11 Hz,1H), 4.58-4.54 (m, 1H), 3.75 (s, 3H), 3.57 -3.56 (m, 2H), 3.06- 2.98 (m, 1H),2.72-268 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  153.7, 142.7, 135.1, 132.6, 129.1, 127.6, 126.6, 126.3, 118.5, 114.4, 78.6, 58.6, 55.3, 42.8, 31.6, 29.4, 25.5.

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Appendix-Chapter 5

<sup>1</sup>H and <sup>13</sup>C NMR Spectra of CDC product


















**Conclusion and Future Outlook** 

#### 6.1 Conclusion

In this thesis we explored the inherent photocatalytic activity of C-dots towards different organic transformations under visible light irradiation. The photo induced electron transfer from C-dots facilitated the decomposition of TBHP which subsequently catalyzed the C-H oxidation of various benzylic hydrocarbons. The photooxidation efficiency of the CDs was highly dependent on the surface functional groups. The carboxyl functionalized CDs showed the best photocatalytic efficiency promoting transfer of photoexcited electrons to reactants and favouring the inhibition of the electron-hole recombination. The acidic behaviour of CDs owing to their surface functionalities could be used as an acid catalyst. Combination of photooxidation and surface acidity of sulphated carbon dots (s-CDs) exhibited dual catalytic properties, where it induced rapid photooxidation of xanthenes in presence of molecular oxygen to form a hydroperoxy intermediate followed by coupling of nucleophiles catalyzed by the acidic surface functional groups. The presence of various functionalities on the surfaces of CDs could also be used for anchoring other active catalysts such as metal and metal oxide nanoparticles. Herein, we demonstrated the efficiency of these CDs in anchoring  $Fe_3O_4$  nanoparticles. The photocatalytic activity of the resulting nanocomposites was studied towards cross-dehydrogenative coupling of N-phenyltetrahydroisoquinoline with nucleophiles under visible light irradiation. We showed that apart from acting as a support, a cooperativity effect between the active catalyst and the support were instrumental in enhancing the photocatalytic activity of the catalyst. It was also observed that CDs could not afford a significant yield with nitrogen group (-NH<sub>2</sub>) containing substrate. It might be due to the formation of photoinduced electron donor acceptor pair with the  $-NH_2$ functionalized substrate molecules.

#### 6.2 Future Outlook

The carbon based nanomaterials have enormous potential either as catalysts themselves or heterogeneous catalyst supports. Various forms of carbon including activated carbon, graphite, fullerenes, carbon nanotubes etc. showed superior surface characteristics that have been explored for the development of hybrid catalytic systems with high and selective activity in chemical-, electro- or

photocatalysis. C-dots is a new member in the nanocarbon family which have widely used in areas like sensing, optoelectronics, bioimaging, nanomedicine, etc. They have been shown to possess advantages over conventional semiconducting photocatalyst in terms of photostability and biocompatibility. Cdots with oxygenated functional groups on their surface could act as active sites for various acid catalyzed and oxidative catalytic reactions under visible light irradiation. Recent advancement of these C-dots based materials shows that the modification of C-dots surface by different methods leads to efficient separation of electron hole pairs  $(e^{-}/h^{+})$  which acts as traps for reactive oxygen species for many challenging organic reactions. Further doping with hetero atoms such as N, P, S, B etc. changes their inherent physico-chemical properties to a large extent. The most important challenge which needs to be accomplished is to provide a definite PL mechanism for C-dots. Only on the basis of understanding of the PL mechanism of C-dots, we can design C-dots with desired properties and can establish an appropriate mechanism for organic reactions. The application of Cdots and their composites in organic transformations is an evolving area and have potential in several areas such as (i) development of chiral C-dots for enantioselective synthesis, (ii) for utilization of  $CO_2$  to valuable fine chemicals, (iii) affordable methods for large scale synthesis, industrial scalability economic viability, (iv) detailed elucidation of photocatalytic mechanism that can bring further improvements in catalytic activity and (v) stability of the catalyst to maintain excellent catalytic activity during recycling. Overall, development of carbon dots as photocatalysts with broader applications is imminent towards green and sustainable chemistry as a replacement of the toxic semiconductor quantum dots.



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