INVESTIGATION OF FLUORESCENCE QUENCHING OF QUANTUM DOTS AND ITS APPLICATION IN PHOTOCATALYTIC ORGANIC TRANSFORMATIONS

ANUUSHKA PAL

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
JANUARY 2017

INVESTIGATION OF FLUORESCENCE QUENCHING OF QUANTUM DOTS AND ITS APPLICATION IN PHOTOCATALYTIC ORGANIC TRANSFORMATIONS

by

ANUUSHKA PAL

Department of Chemistry

Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the

Indian Institute of Technology Delhi

January 2017

Dedicated to
My grandfather &
My Parents

CERTIFICATE

This is to certify that the thesis entitled, "**INVESTIGATION OF FLUORESCENCE QUENCHING OF QUANTUM DOTS AND ITS APPLICATION IN PHOTOCATALYTIC ORGANIC TRANSFORMATIONS**" being submitted by **Ms. ANUUSHKA PAL** to the **Indian Institute of Technology Delhi** for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of bonafide research work carried out by her Ms. ANUUSHKA PAL has worked under my guidance and supervision. She has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

Date

Dr. SAMEER SAPRA
ASSOCIATE PROFESSOR
DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
NEW DELHI-110 016

ACKNOWLEDGEMENTS

I joined the "**Nanogroup**" six years ago. It has been a long time in this lab and my journey would be incomplete without acknowledging the people who have not only nurtured me in scientific skills but at the same time also helped me in developing personally too.

First of all, I would like to thank and express my gratitude to my supervisor **Dr. Sameer Sapra,** IIT Delhi for opening my eyes to the scientific challenges and to develop the critical thinking over the scientific issues. He is very supportive and motivational towards the scientific hurdles that I faced during my projects. His methodological approach, unconditional support, friendliness and jovial nature has created the competitive yet vibrant and stress free work environment that ultimately has helped me to learn and love research more and more. I am extremely privileged to work under his guidance and after long scientific discussions and arguments!!! This thesis has come to an end. 

I wish to convey my warm regards and offer my heartfelt thanks to **Prof. Burkhard Koenig**, Universität Regensburg, Germany for giving me opportunity twice to work in his lab through scholar exchange visits. It was my pleasure to learn from him during the subgroup and group discussions. I am extremely impressed by his punctuality, time management, organized approach and dedication towards science. I want to adopt all these good habits into my present and future scientific endeavours. I am also thankful to Dr. Petra Hilgers for providing the details of iPUR exchange programme and guiding me in handling administrative issues.

My sincere and heartfelt thanks to our collaborator Dr. Jyotishman Dasgupta, TIFR, Mumbai, for his guidance in understanding the concepts of ultrafast spectroscopy and extending his lab facilities to me. His passion and curiosity for science has always inspired me to go in depth of scientific problem and learn as much as I can and at same time start building lateral thinking. His theory of scientific discussion at any time anywhere has made me discussion freak and developed love for science.

I would like to thank Prof. G.Krishnamoorthy, TIFR Mumbai for teaching me the concepts of TCSPC and extending his lab facilities to me.

I also wish to extend my sincere thanks to Dr. Rajeev Gupta, University of Delhi for collaborated research projects for providing the cobalt complexes, valuable time and thoughtful advice during the manuscript preparations. I am extremely thankful to Sumit for carrying out the synthesis of cobalt complexes and for useful suggestions.

I am extremely thankful to Dr. Pramit Chowdhury, Dr. Shashank Deep and Dr. Pravin P Ingole for providing me various characterization facilities that have contributed immensely towards my research work.

I am thankful to the SRC members Prof. B. Jayaram, Dr. Shashank Deep and Dr. Shantanu Ghosh for their encouragement and constant support. I express my deep sense of grattiture to present head of department Prof. Ravi Shankar and former heads of the department for providing me all the facilities.

It is my pleasure to express gratitude and heartfelt thanks to my awesome lab mates who have immensely contributed toward this thesis. Their round the clock support and unbroken bond of friendship has provided me mental strength, motivation, zeal, entertainment and competitive research environment. First of all, I would like to thank my senior colleagues Dr. Udit Soni and Vikas Arora for their warm affection, support during the tough times and healthy scientific interactions. I am blessed to have an awesome colleague as well as a good friend Sushma for her involvement, 24x7 hour help have converted my research life into a memorable journey. I would also like to thank my junior colleague Samim for his gentle nature, constant support and exhaustive discussions about new scientific problems and their future aspects. Thanks are also extended to Dr. Gurpal, Mona, Mamata, Dr. Puspanjali, Dr. Atanu, Dr. Arpita, Rusha, Sajan, Dr. Aditya, Liza, Pallavi, Razi and not to forget Ankur, Manzoor, Preeti, Sulekha, Amitrajit, Suraj, Meenu, Apurba, Khushboo, Vivek, Prateek, Bhawna, Baristar, Naveen, Jai Ganesh, Shambhavi, Hemaa, Shantanu, Shreya, Diksha, Nikita, Siddharth, Krishna, Tanya, Buban, Preeti, Beena, Divya, Akansha, Satya and Ajeet.

I would like to thank the people who have made my stay wonderful and memorable in Germany. My special thanks to my landlady Beate for accommodating me in her beautiful house. She was very friendly, helpful and treated me like her daughter. Scientific work would not be so enjoyable without the support of the technical staff and labmates at Universität

Regensburg. I would like to thank technical staff of Koenig group Viola, Britta, Regina, Rudi, Ernst and Simone for their administrative support, technical assistance in reaction set ups and instrumentation facilities. I have been shuffling from one lab to another lab in my 6 months tenure. Therefore, I got a chance to interact with each and every member of the biggest group of Chemistry department. There is a long list of people whom I would like to appreciate and thanks. First of all, I would mention the name of Martin, my first lab partner known as Fruity for his fruity nature, very supportive and caring. Caroline for sharing her fumehood with me and as well as my stress buster and gossip partner. Willi and Tamal for sharing laughter moments and lively environment in the lab. Thea, Swarupa, Amrita, Anna, Thomas, Durga, Anika, Dr. Rizwan and Dr. Leyre for scientific and non scietinific discussions at Koenig's kitchen. I would like to thank Dr. Indrajit for long scientific discussions, developing my project and helping me in understanding my project more deeply.

I would also acknowledge the amazing people I met at TIFR Mumbai, without whom stay at TIFR would be boring. First of all, I would like to thank Dr. Ajay and Dr. Rahul for their cooperation and Dr. Ajay for carrying out ultrafast absorption spectroscopy measurements. I would like to thank Anju and Rustam for taking care of me during my first visit at TIFR. I will never forgot my tea time buddies Kshama, Palas, Ankita and my awesome friend Vijayalakshmi for night gossips in the canteen. The cherishing moments during the walk at seashore, listening Joel's stories and watching late night movies shows after work are unforgettable.

Words fail to express my sincere thanks to all of my friends at IIT Delhi. Life in IIT Delhi would have remained charmless without all my pretty wonderful friends. Their friendship has made my life colorful and enjoyable. I am lucky to have friends like Sushma, Sara, Amita, Preeti and Meenal

I gratefully acknowledge the immense assistance, persistent encouragement received from my friends Ritika, Hari, Jyoti, Annu, Shweta and Jolly. The root of joy and self confidence in me owe to them.

I would like to appreciate all the administrative and instrumentation lab staff for their cooperation and help.

I would like to acknowledge the financial assistance received from “UGC” which has made my PhD work possible over here. I would also like to thank DFG, German funding agency and iPUR fellowship from DAAD for providing financial assistance for my stay at Germany.

My family members have played a vital role in shaping my thesis and their constant love & support, motivation, persistent confidence on my abilities cannot be described in words. I am extraordinarily fortunate to have the blessings of my grandfather **Shri Gokul Pal**. My mother, **Smt. Kranti Pal** is the one who always blessed me with the shower of her care and love. She is my role model and always inspired to move ahead in life. My father, **Shri Rohtash Kumar Pal** is my first “Guru” (teacher), who put high moral values inside me and makes me strong enough to face any obstacle in life. My caring elder brothers (**Jitender** and **Sonu**) are pillar of my strength and always guided me personally and professionally to handle the hurdles in life. I would like to thank my bhabhi (**Pooja** and **Shamita**) for their unconditional love and infusing faith in me that I could do good science. I would like to thank my sister (**Lalita**) and my jiju (**Mahesh**) for their inspirational quotes and words. I would like to thank my naughty nephews (**Yuval, Sparsh** and **Madhav**) known as packet of energy, pranksters and stress buster for me at home.

I must definitely thank my sweet hubby **Dr. Parveen Saini** for his love, patience, encouragement and constant support. He is real mentor to me and pushed me beyond my capabilities to do work impeccably. He is my biggest critics too and answering his questions is challenging and pain bearing tough task for me. I would like to appreciate and thank my in laws for their faith in my abilities and being patient inspite of spending very less time with them.

At last but not the least I would like to thank almighty **God** for showing me the right path in life.

ANUUSHKA PAL

ABSTRACT

Semiconductor nanocrystals (NCs) or quantum dots (QDs) have attracted much attention in recent decades due to their novel electronic/optical properties and wide range of dependent applications in the areas like photovoltaics (PVs), light emitting diodes (LEDs), photocatalysis, bioimaging, biosensing, cancer treatment etc. QDs represent class of semiconductors based on elements of groups II-VI, III-V, or IV-VI of periodic table (e.g. CdSe, CdS, CdTe, ZnS, InP etc.) with size comparable to the Bohr exciton radius, thereby showing size dependent optical, electronic and chemical properties. It is known that the applicability of QDs in the above areas and related performance indices (e.g. efficiency) are governed by the structural features of QDs and various processes (e.g. energy transfer, electron/hole transfer, back electron transfer, heat dissipation), which determines the fate of photogenerated excitons. Interestingly, the fluorescence of QDs is highly dependent on above processes; therefore, quenching or reduction pattern of fluorescence intensity carries information about involved processes and is worth investigating. The present thesis is mainly focused on designing of core only or core/shell heterostructured QDs and investigation of their fluorescence quenching mechanism in the presence of Co (III) complexes, to highlight the involved static (e.g. ground state complex formation or proximally placed fluorophore/quencher) or dynamic quenching (e.g. collisional quenching, energy/charge transfer etc.) sub-processes. The role of size of QDs, nature of complexes, effect of shell thickness, electrostatic interactions between QDs & complexes have also been investigated. Finally, the suitably designed core/shell QDs have demonstrated for photocatalytic carbon-carbon coupling reactions with elucidation of exciton dynamics and catalysis mechanism. Accordingly, the entire thesis has been divided into the eight chapters as described below. The first two chapters introduce the reader to the existing literature and the

methods used. The systematic study starts with establishing the possibility of fluorescence quenching of CdSe/ZnS QDs by Co(III) complexes (Chapter 3) which is then taken further by evaluating the effects of the QD size (Chapter 4) and the thickness of the ZnS shell (Chapter 5) on the quenching mechanisms and efficiency. The interaction of the Co(III) complexes with the QDs leads us to examine the possibility of forming extended assemblies using this combination as reported in Chapter 6 and the possibility of the charge transfer enables us to use the QDs for photocatalytic organic transformations (Chapter 7). The thesis is summarized in Chapter 8.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SCHEMES

GLOSSARY OF SYMBOLS AND ABBREVIATIONS

%	percent
ν	frequency
Å	angstrom
µL	microlitre
°C	degree centigrade
nm	nanometer
EDX	energy dispersive X-ray analysis
e.g.	for example
g	gram
hr	hour
Hz	hertz
i.e.	that is
kV	kilovolt
eV	electron volts
M	molar
mmol	millimole
µM	micromolar
mol	mole
mL	milliliter
ns	nanosecond
nm	nanometer
NP	nanoparticle
SNMs	semiconductor nanomaterials
NCs	nanocrystals
TEM	transmission electron microscopy
HR	high resolution
PXRD	powder X-ray diffraction
DIPEA	diisopropylethylamine
BrBN	bromobenzonitrile