

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

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by

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Submitted

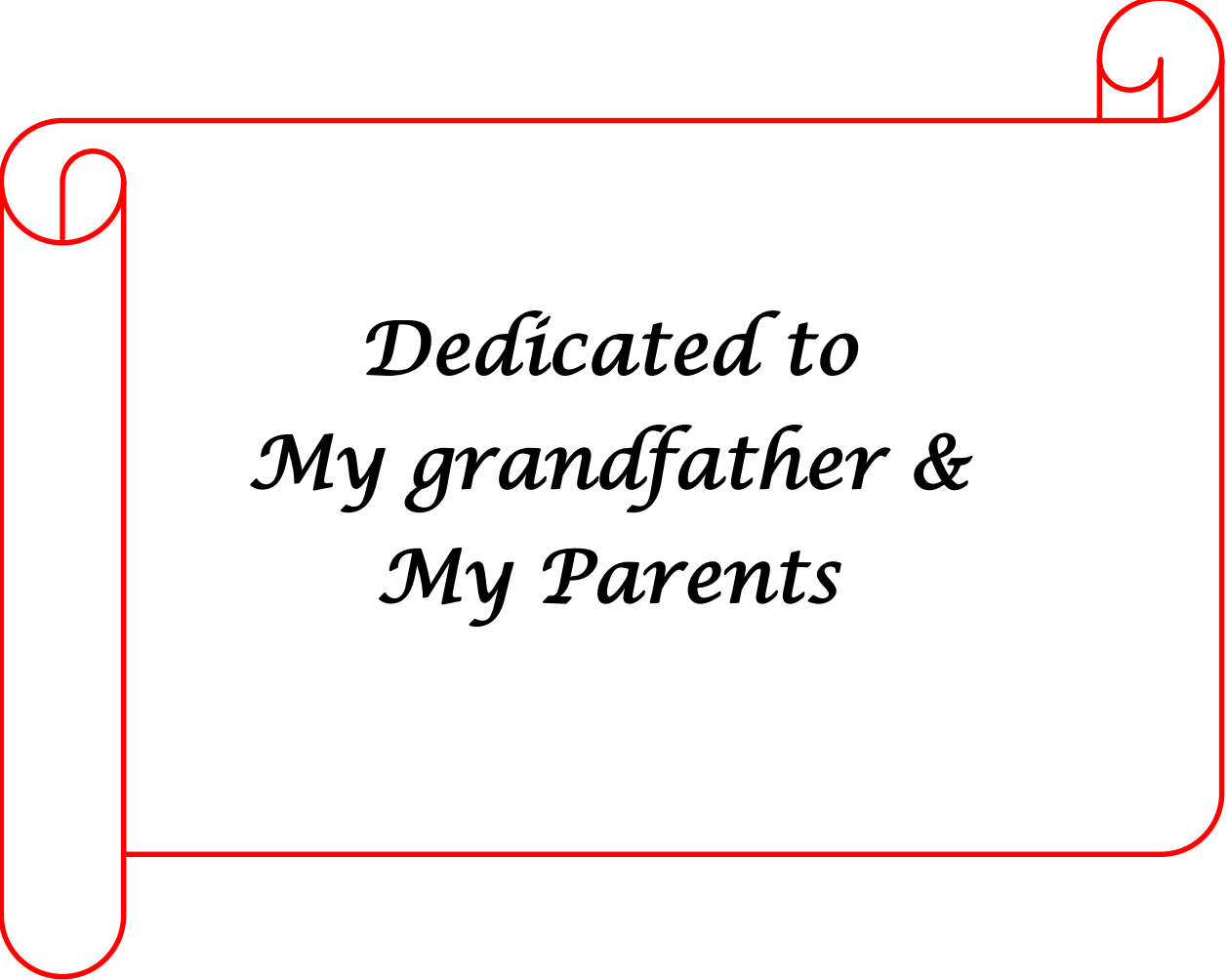
in fulfillment of the requirements of the degree of Doctor of Philosophy

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.

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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.

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GLOSSARY OF SYMBOLS AND ABBREVIATIONS

%	percent
ν	frequency
Å	angstrom
μL	microlitre
$^{\circ}\text{C}$	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