# Aromatic Sulfonium Polyoxometalates as Photochromic Materials and Self-separating Catalysts

A Thesis

Submitted for the Degree of

DOCTOR OF PHILOSOPHY

In the School of Basic Sciences

By

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Dedicated
To
"All My Loved Ones"

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# Declaration by the Research Scholar

I hereby declare that the entire work embodied in this Thesis is the result of investigations carried out by me in the ***School of Basic Sciences***, Indian Institute of Technology Mandi, under the supervision of ***Dr. Pradeep C. Parameswaran***, and that it has not been submitted elsewhere for any degree or diploma. In keeping with the general practice, due acknowledgements have been made wherever the work described is based on finding of other investigators.

Place: Kamand (Mandi) Signature:

Date: Name: Ashwani Kumar

# Declaration by the Research Advisor

I hereby certify that the entire work in this Thesis has been carried out by Mr. Ashwani Kumar, under my supervision in the School of Basic Sciences, Indian Institute of Technology Mandi, and that no part of it has been submitted elsewhere for any Degree or Diploma.

Signature:

Name of the Guide: Dr. Pradeep C. Parameswaran

Date:

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**Ashwani Kumar**

# Table of Contents

# Abbreviations

## Symbols

| | |
|---|---|
| $\lambda_{max}$ | Reflectance value before irradiation |
| B | Salient coloration kinetic parameter |
| a, b | Coloration kinetic parameters for the linear relation |
| $\delta$ | Chemical Shift |
| $t_{1/2}$ | Half Life Time |
| $E_g$ | Energy Gap |

## Solvents

| | |
|---|---|
| $CHCl_3$ | Chloroform |
| $CH_2Cl_2$/DCM | Dichloromethane |
| DMF | Dimethylformamide |
| DMSO | Dimethylsulfoxide |
| EtOH | Ethanol |
| MeOH | Methanol |
| TEA | Triethylamine |
| THF | Tetrahydrofuran |
| ACN | Acetonitrile |

## Chemicals

| | |
|---|---|
| PhBr | Bromobenzene |
| EO | Ethyl oleate |
| MO | Methyl oleate |

## Instruments

| | |
|---|---|
| $^{13}$C NMR | Carbon Nuclear Magnetic Resonance |
| $^{1}$H NMR | Proton Nuclear Magnetic Resonance |
| $^{31}$P | NMR Phosphorus Nuclear Magnetic Resonance |
| HR-MS | High Resolution Mass Spectrometry |

| | |
|---|---|
| ESI-MS | Electron Spray Ionization Mass Spectrometry |
| FT-IR | Fourier Transform Infrared Spectroscopy |
| DSC | Differential scanning microscopy |
| SCXRD | Single Crystal X-Ray Diffraction |
| GC | Gas Chromatography |
| DRS | Diffuse Reflectance Spectroscopy |
| UV-Vis | Ultraviolet-Visible |
| FID | Flame Ionized Detector |

**Others**

| | |
|---|---|
| TLC | Thin Layer Chromatography |
| TMS | Tetramethylsilane |
| μM | Micro-molar |
| mM | Milli-molar |
| nM | Nano-molar |
| $^{o}C$ | Degree Celsius |
| CCDC | Cambridge Crystallographic Data Center |
| HOMO | Highest Occupied Molecular Orbital |
| LUMO | Lowest Unoccupied Molecular Orbital |
| PPM | Parts Per Million |
| pH | Potential of Hydrogen |
| EDG | Electron Donating Group |
| EWG | Electron Withdrawing Group |
| ORTEP | Oak Ridge Thermal-Ellipsoid Plot |

## Abstract

The design and development of molecular materials that exhibit two or more properties of interest are gaining attention in recent years. These materials are often built on platforms like metal nanoparticles, metal organic frameworks, polymeric materials, and nanocomposites. Polyoxometalates (POMs), discrete, anionic metal oxide clusters of early transition metal ions, represent a vast class of inorganic materials possessing enormous diversity in their size, structure and properties which make them suitable in the field ranging from optical, magnetic, catalytic, biological and electronic applications. It is well-known that the properties of a hybrid POM can be engineered by systematically varying its organic counterions. These organic counterions can be fine-tuned through various substitutions like change of functional group, by introducing electron releasing and electron withdrawing group on the substituents, increasing the resonance in organic molecule or increasing and decreasing of chain length. The present thesis is focused on the two diverse materials properties of the POM organic hybrids. These properties are photochromism and self-separating catalysis.

POMs owing to their ability to accept and release electrons make them attractive compounds for the development of photochromic materials. In POM-based photochromic materials, the photo-excitation leads to electron transfer from the cluster oxygen to metal ion generating reduced metal centers. The reduced metal centers in turn lead to the coloration of the material through various electronic transitions. In this regard, the organic counter cations of the anionic POM cluster play significant roles in deciding the photochromic properties of a POM-hybrid. Organoammonium cations (OACs) are the common class of cations used in POM chemistry and a vast majority of the known photo-chromic POM materials are those containing OACs.

Meanwhile, self-separating catalysts, which combine the properties of homogeneous and heterogeneous catalysts in a single entity, are becoming important in many industrial applications. It has advantages of both heterogeneous catalysts which include easy separation and recyclability, and homogenous catalysts which offer relatively high activity and improved