

Synthesis and Physicochemical Characterization of Visible-Light Absorbing Rhenium-Based Complexes

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in partial fulfillment of the requirements for the Degree of**

DOCTOR OF PHILOSOPHY IN CHEMISTRY

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Synopsis

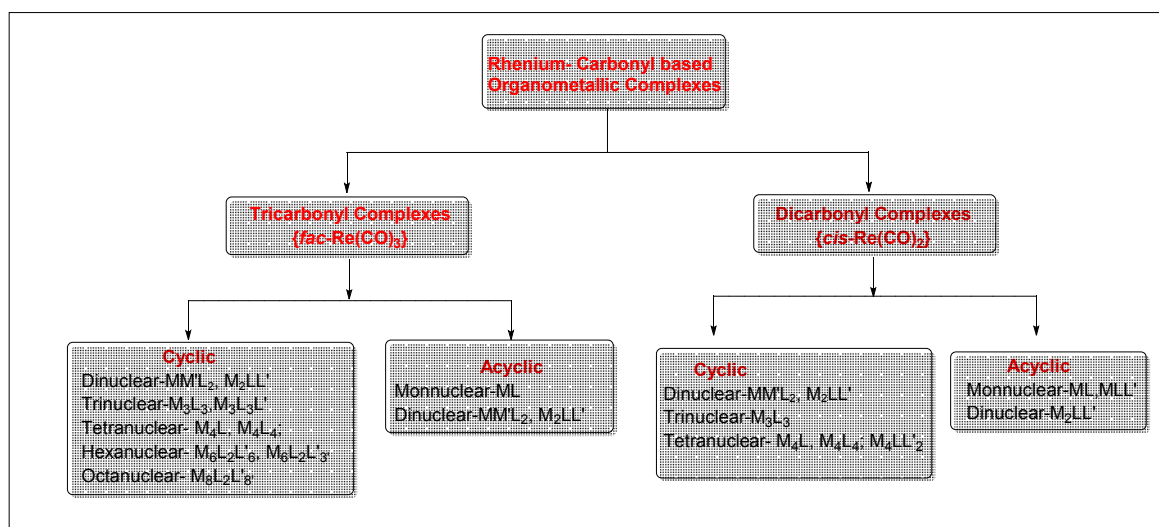
This thesis entitled “**Synthesis and physicochemical characterization of visible light absorbing rhenium-based complexes**” comprises of six chapters. The first chapter describes the **General Introduction** and **References** on rhenium based carbonyl complexes and their applications. The second, third, fourth and fifth chapters have been subdivided into five sections namely **Introduction, Experimental Section, Results and Discussion, Conclusions** and **References**. The work described in the present thesis would explore the syntheses and characterization of rhenium carbonyl based organometallic complexes.

Chapter-1

Introduction

The present chapter deals with the general introduction of rhenium-carbonyl based complexes that include their overall classification, different types of synthetic routes and strategies, the literature survey starting from their discovery to current scientific applications, *etc.* Variety of rhenium carbonyl-based complexes consisting of mono, di, tri, tetranuclear and their synthesis, structural characterization were described shortly. The **(Scheme 1)** describe the general classification of rhenium-carbonyl based organometallic complexes in the literature. In brief, the present chapter brings an idea about the basic principles involving in assembling tri/di carbonyl ligands into cyclic/acyclic Re(I)

complexes. The literature background supports the photophysical properties of Re(I) complexes that can be tuned by proper designing of the coordination environment.



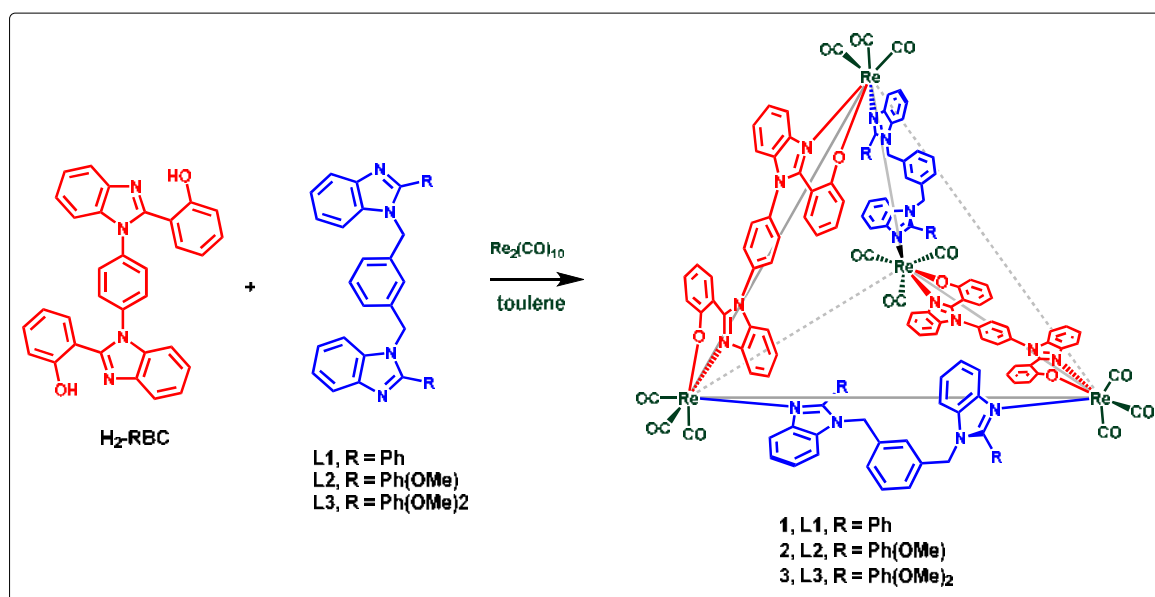
Scheme 1. Flow chart showing the general classification of rhenium carbonyl based organometallic complexes.

Chapter-2

Syntheses and characterization of *fac*-Re(CO)₃-based neutral heteroleptic tetrahedrons

Two new flexible ditopic nitrogen donors possessing xylene spacer and 2-phenylbenzimidazolyl or its derivatives as coordinating unit were synthesized and further used with rigid bis-chelating ligand and Re₂(CO)₁₀ for making new family of neutral, heteroleptic tetrahedral shaped supramolecular coordination complexes *via* one-pot approach (**Scheme 2**). The new ligands and the complexes were characterized using various analytical and spectroscopic methods. The molecular structure of the complexes (**1-3**) were determined using single crystal X-ray diffraction analysis which reveal that four rhenium cores are arranged in the vertices, and four ligands are in the edges of the

tetrahedron. The UV-Vis absorption and emission properties of the complexes **1-3** were investigated in solution THF. All the complexes show UV-Visible electronic absorption in the range of 350 – 450 nm and significant molar absorption coefficient (ϵ) in the range of 36088 - 39741 $\text{M}^{-1}\text{cm}^{-1}$.



Scheme 2. Synthesis of complexes **1-3**

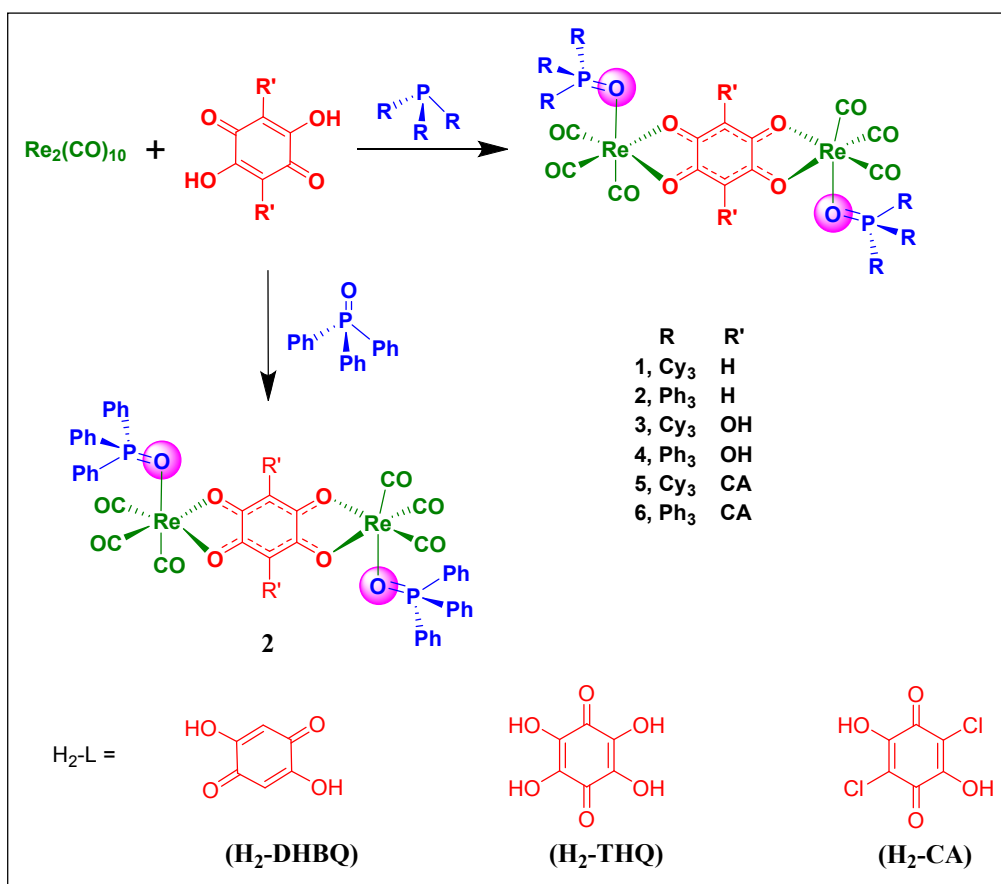
Chapter-3

Phosphine-donor based tricarbonylrhenium(I) complexes from phosphine/phosphine oxide and dihydroxybenzoquinones

Neutral phosphine oxide (P=O) donor based organometallic complexes $[\{\text{Re}(\text{CO})_3\text{O}=\text{PCy}_3\}\{\mu\text{-DHBQ}\}\{\text{Re}(\text{CO})_3\text{O}=\text{PCy}_3\}]$ (**1**), $[\{\text{Re}(\text{CO})_3\text{O}=\text{PPh}_3\}\{\mu\text{-DHBQ}\}\{\text{Re}(\text{CO})_3\text{O}=\text{PPh}_3\}]$ (**2**), $[\{\text{Re}(\text{CO})_3\text{O}=\text{PCy}_3\}\{\mu\text{-THQ}\}\{\text{Re}(\text{CO})_3\text{O}=\text{PCy}_3\}]$ (**3**), $[\{\text{Re}(\text{CO})_3\text{O}=\text{PPh}_3\}\{\mu\text{-THQ}\}\{\text{Re}(\text{CO})_3\text{O}=\text{PPh}_3\}]$ (**4**), $[\{\text{Re}(\text{CO})_3\text{O}=\text{PCy}_3\}\{\mu\text{-CA}\}\{\text{Re}(\text{CO})_3\text{O}=\text{PCy}_3\}]$ (**5**), and $[\{\text{Re}(\text{CO})_3\text{O}=\text{PPh}_3\}\{\mu\text{-CA}\}\{\text{Re}(\text{CO})_3\text{O}=\text{PPh}_3\}]$ (**6**)

were assembled from phosphine/phosphine oxide, dihydroxybenzoquinone donor and $\text{Re}_2(\text{CO})_{10}$ via one-pot solvothermal approach (**Scheme 3**). The soft phosphine donor was transformed into hard phosphine oxide donor *in situ* during the formation of **1**, **3**, **4**, **5**, and **6**. The commercially available phosphine oxide was used for the preparation of complex **2**. The complexes **1-6** are air and moisture stable and are soluble in organic polar solvents. The complexes were characterized by elemental analysis, FT-IR, NMR spectroscopic methods. Molecular structure of **1**, **2**, **4**, **5**, and **6** were analyzed by single-crystal X-ray diffraction analysis.

All the complexes strongly absorb visible light in the region of 350-700 nm. The molar absorption coefficient was calculated for all the complexes and compared. Interesting photophysical behavior has been observed for complexes **5** and **6**. The molar absorption coefficient of complex **5** ($34,719 \text{ M}^{-1}\text{cm}^{-1}$) and **6** ($33,965 \text{ M}^{-1}\text{cm}^{-1}$) proves that the complexes are one among the rare examples of reported in the literature having a significant absorption coefficient. The electron withdrawing nature of chlorine group substitution in the chelating unit (CA) plays a vital role in the electronic transition of complexes **5** and **6**. In order to bring insight into the electronic transition Time dependant density functional theory (TDDFT) also performed and discussed in brief. The results reveal that change from N donor to P donor as well as in the P=O donor based cyclic SCCs to P=O donor-based acyclic complexes increased the molar absorption coefficient. This approach provides a way to synthesize acyclic complexes using P/P=O donor- based ligands with moderate/strong absorption in the visible region.



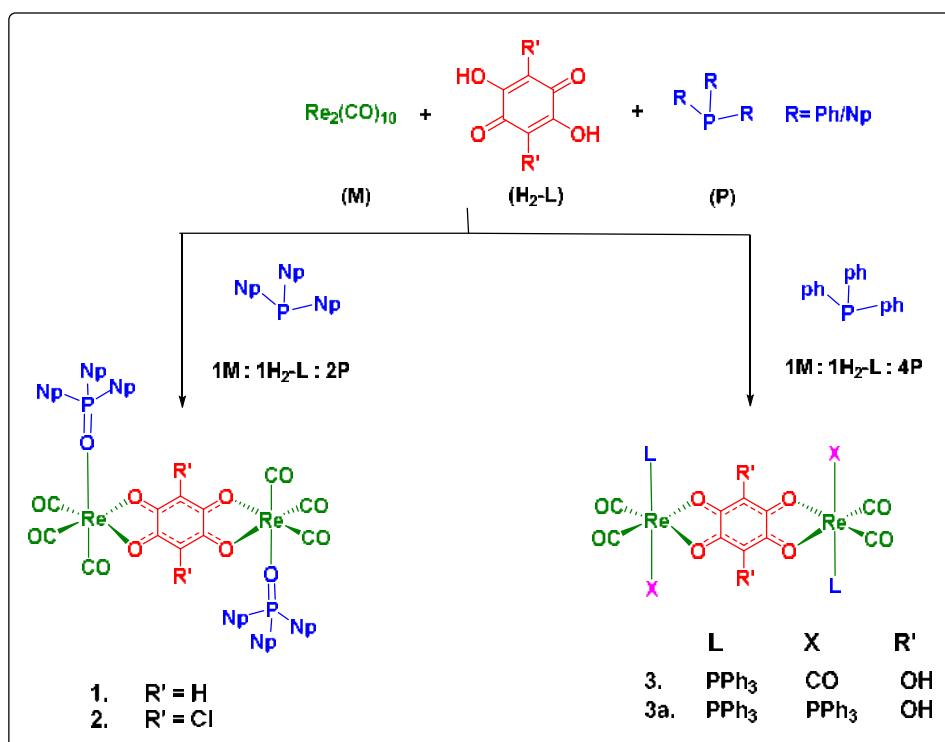
Scheme 3. Synthesis of complexes 1-6

Chapter-4

Stoichiometrically controlled syntheses and structural characterization of phosphine oxide / phosphine coordinated dinuclear rhenium(I) tricarbonyl complexes

Tri/dicarbonylrhenium based complexes using neutral phosphine oxide/phosphine (P=O/P) coordinated rhenium based organometallic complexes [(O=PNp₃)Re(CO)₃(μ-L)Re(CO)₃(O=PNp₃)] (**1**, H₂-L = H₂-DHBQ = 2,5-dihydroxy-1,4-benzoquinone, PNp₃ = tri-1-naphthylphosphine) and (**2**, H₂-L = H₂-CA = 2,5-dichloro-3,6-dihydroxy-p-

benzoquinone); [(PPh₃)Re(CO)₃(μ-THQ)Re(CO)₃(PPh₃)] (**3**, H₂-THQ = tetrahydroxy-1,4-benzoquinone, PPh₃ = triphenylphosphine) and [(PPh₃)₂Re(CO)₂(μ-THQ)Re(CO)₂(PPh₃)₂] in **3a**, were synthesized from phosphine/ phosphine oxide, a bis-chelating oxygen donor (H₂- DHBQ/ H₂-CA/ H₂-THQ) and Re₂(CO)₁₀ *via* a one-pot solvothermal synthetic approach (**Scheme 4**). The complexes were characterized by ATR-IR, ESI-Mass and NMR spectroscopy. The precise molecular structures of complexes **2-3** and **3a** were unambiguously determined by single crystal X-ray diffraction analysis. The stoichiometrically controlled syntheses route has been established as of 1:2 and 1:4 equivalent of rhenium precursor and phosphine donor respectively. Phosphine oxide coordinated complexes **1** and **2** demonstrate UV-Visible absorption in the range of 350 -700 nm.

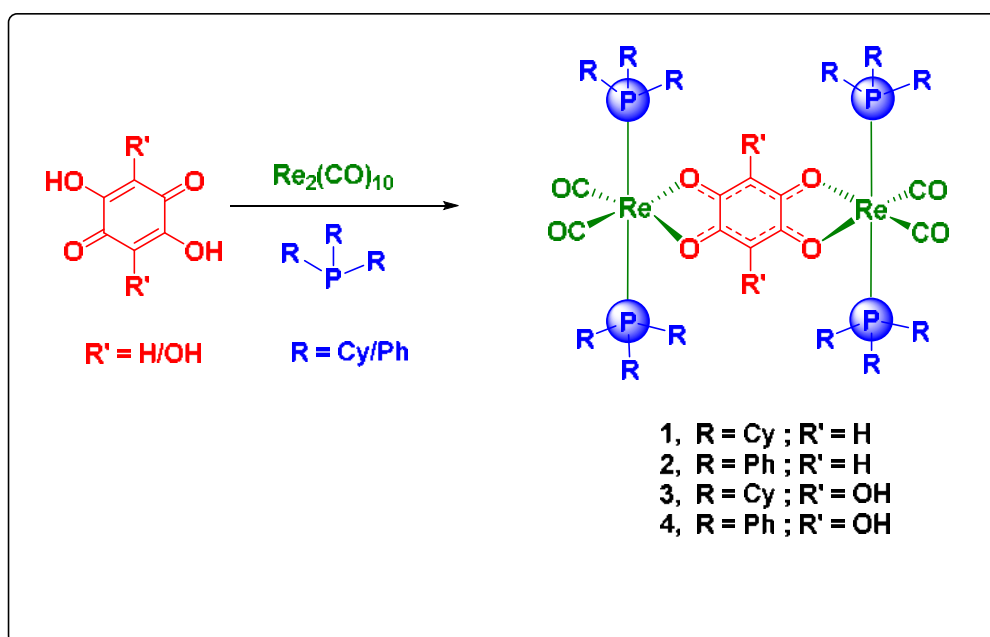


Scheme 4. Synthesis of complexes **1-3** and **3a**

Chapter-5

Stoichiometrically controlled syntheses and structural characterization of phosphine coordinated dinuclear rhenium(I) dicarbonyl complexes: Comparison of cyclic and acyclic structural features

A new class of neutral phosphine donor-based organometallic rhenium dicarbonyl complexes $[(PR_3)_2Re(CO)_2(\mu\text{-DHBQ})Re(CO)_2(PR_3)_2]$, $L = \mu\text{-DHBQ} = H_2\text{-DHBQ} = 2,5\text{-dihydroxy-1,4-benzoquinone}$, (**1**, $PR_3 = PCy_3 = \text{tricyclohexylphosphine}$) and (**2**, $PR_3 = PPh_3 = \text{triphenylphosphine}$); $[(PR_3)_2Re(CO)_2(\mu\text{-THQ})Re(CO)_2(PR_3)_2]$, $L = \mu\text{-THQ} = H_2\text{-THQ} = \text{tetrahydroxy-1,4-benzoquinone}$, (**3**, $PR_3 = PCy_3 = \text{tricyclohexylphosphine}$) and (**4**, $PR_3 = PPh_3 = \text{tri-phenylphosphine}$) were synthesized from phosphine/ phosphine oxide, a bis-chelating oxygen donor ($H_2\text{-DHBQ}/ H_2\text{-THQ}$) and $Re_2(CO)_{10}$ via a one-pot solvothermal synthetic approach (**Scheme 5**). The complexes were characterized by ATR-IR, ESI-Mass and NMR spectroscopy.



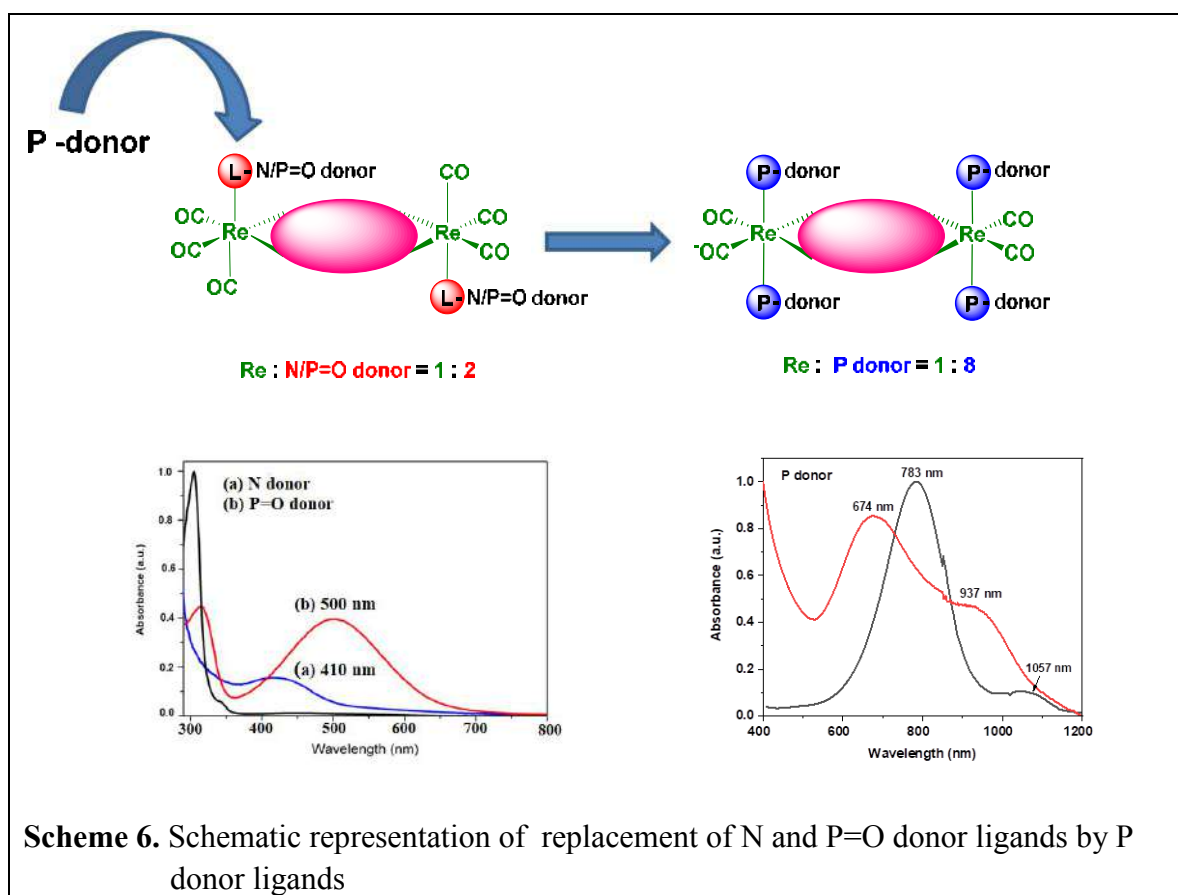
Scheme 5. Synthesis of complexes 1-4

The precised molecular structure of complexes **1-4** were unambiguously determined by single crystal X-ray diffraction analysis. The stoichiometrically controlled syntheses route has been established as of 1:8 equivalent of rhenium precursor and phosphine donor respectively. Important structural features of our previous report of cyclic P=O donor based rhenium-tricarbonyl complex was compared with the present work of acyclic P=O donor based rhenium-tricarbonyl (chapter 4) and acyclic P donor based rhenium-dicarbonyl (chapter 5). Complexes **3** and **4** demonstrate UV-visible-near IR absorption in the range of 450 – 1200 nm. The result clearly indicates that the electronic absorption property of the rhenium complex simply could be altered by appropriate design and choice of ligand.

Chapter-6**Summary and Conclusion**

In summary, rhenium(I) based both tri/di carbonyl bonded organometallic complexes were synthesized by one-pot approach of the solvothermal method. In the entire complexes, the rhenium metal center was noticed as dinuclear. In all the chapters, the structural topology was observed as acyclic except in chapter 2 where cyclic complexes were reported. The important structural features of cyclic and acyclic complexes were compared for their better clarity. All the complexes were characterized by using available analytical instruments such as UV-Visible-Near IR, ATR-IR, and NMR spectroscopy. The exact molecular structure of complexes were unambiguously

determined using single crystal X-ray crystallography. The photophysical properties of complexes were investigated and compared using UV-Visible spectroscopy. Some of the complexes reported in the present work were perceived with an excellent molar absorption coefficient. Additional evidence for the electronic transition was produced by TDDFT studies. In conclusion, the electronic absorption property of rhenium complexes was tuned to an extent of N-donor ligands (UV region, our previous report) to P=O donor (UV-Visible region, chapter 3 and 4) furthermore to P donor (UV-Visible-Near IR, chapter 5). A pictorial representation showing the stepwise shifting of UV-Visible electronic absorption starting from N-donor ligands to P=O donor and further to P donor ligands has been shown in **Scheme 6**.



Various synthetic routes were established for the successful isolation of rhenium(I) dinuclear complexes. To the best of our knowledge, such systems are highly useful in material chemistry and biological applications. The present work opens a new pathway to explore the synthesis which further can be extended to make stable supramolecular assemblies with various size/shapes exhibiting interesting photophysical properties.