1
Introduction

"Formalisms are convenient fictions which contain a piece of the truth"

-Roald Hoffmann[Saillard et al., 1984]

Alfred Werner (1913: Nobel Prize in chemistry), popularly known as the father of coordination chemistry, has developed the basis for modern coordination chemistry theory applicable to various transition metal complexes. The classic Werner complexes: $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_3Cl_3]$, *trans*-$[Co(NH_3)_4Cl_2]$, etc. are the model examples defining ligand's innocence in the metal complexes. Indeed, the innocent nature of the ligands in a *cis*-$[Co(NH_3)_4Cl_2]$ complex allowed Werner to confidently assign the +2 oxidation state to the central cobalt metal ion. Contrary to that, in the early 1960s, a series of nickel dithiolene complexes were recognized to exhibit ligand-centered non-innocent behaviour [Dzik et al., 2011; Jørgensen, 1966a]. Such non-innocent behaviour has led to an imprecise oxidation state of nickel metal, subjected to the uncertainty of the dithiolene ligand being in the oxidized or reduced form [Baker-Hawkes et al., 1966; Eisenberg et al., 2011]. Jørgensen in 1966 coined the term "non-innocent" ligands for such ligands where an ambiguity or uncertainty in the oxidation state of metal could suffice. Furthermore, he suggested the use of formal charges on metal ions instead of oxidation states while defining the complexes bearing non-innocent ligands. Later, Chirik added that the experimental (EPR, XPS, etc) and computational studies are often advantageous to appropriately assign the oxidation state of the coordinated metal ion [Chirik, 2011a]. Many of the literature reports consider the terms "non-innocent" and "redox-active" as synonyms for defining a ligand category, whereas, Chirik suggested few distinctions can be made in the two terms. Chirik emphasized that the redox-active ligands may show ambiguous character, with a clearly defined oxidation state during the chemical reactions [Chirik, 2011b]. Also, the literature over the past six decades covers multiple reports where a non-innocent ligand is capable of manifesting a well-defined redox process, and therefore called as a redox-active ligand [Nakada et al., 2022].

1.1 Redox-active Ligands: An Inspiration from Nature

The presumption for a metal complex containing a redox-inactive ligand dictates that the reduction and oxidation events are metal-centered. Alternatively, for a redox-active ligand, there is a probability for the ligand to be the source and sink of electrons, thereby preventing any unfavorable redox reaction from taking place at the metal center [Kaim, 1987]. A similar strategy has been employed in nature since the beginning of life on Earth, where redox-active organic moieties when combined with 3d transition metals have promoted multi-electronic transformations [Praneeth et al., 2012]. Metalloenzymes in nature rely on redox-active organic or inorganic units, which are either directly coordinated to the metal center, or as a metal cofactor in the second coordination sphere [Rakowski Dubois et al., 2009]. Nature typically lowers the high activation barriers by breaking down the energy demanding redox transformations into multiple straightforward steps. To successfully address such redox reactions, nature has well-developed redox systems in the form of enzymes to catalyze various chemical transformations [Rakowski Dubois et al., 2009]. The biologically active site of these enzymes can be redox-active ligands, amino acids, and metal-clusters. Chart 1.1 displays some of the well-known prosthetic groups present in the biologically active site.

On the other hand, the well-known multielectron reactions in scientific laboratories have long been perceived by precious metals (Pd, Pt, Ir, etc.), as they are typically known for ±2 e^- change in their formal oxidation states [Luca et al., 2013]. Nevertheless, as a consequence of the limited

worldwide reservoirs, precious metals have limited supply, and the significant rise in their price has gathered the research interest of scientists towards the base metal substitutes. Since the base metals tend to undergo ±1 e- change in their oxidation states, few reports suggested a plan to combine two of the ±1 e- changes on base metals to mimic the precious metal redox characteristics. Base metals, such as cobalt can show different oxidation states (Co^{I}, Co^{II}, and Co^{III}) and one can propose the possibility of two successive ±1 e- changes as an acceptable alternative to noble metals. However, this approach invloves the formation of radical species localized over base metals after the first electron transfer process from the substrate during a chemical reaction [Partenheimer, 1995; Petrouleas et al., 2005]. Fast interception of these substrate-derived radicals can make the reaction favorable in the direction as planned, but in most cases, such radicals generate unnecessary side-products [Petrouleas et al., 2005]. The disadavantages of this approach prompted Wieghardt and Chirik to discuss such a possibility to be achieved by bringing redox-active ligands into the account. The redox-active ligand can sustain 1 e- change along with accompanying the 1 e- change at the base metal, giving a total of ±2 e- changes in an overall reaction [Chirik et al., 2010]. Indeed, redox-active ligands are therefore of growing interest for preparing smart base metal complexes to mimic the noble metal characteristics. They constitute a vast pool of multifunctional ligands, with applications in all the domains of chemical and physical sciences [Nakada et al., 2022]. Several roles played by redox-active ligands are shown in Chart 1.2. The detailed classification is given in section 1.1.1.

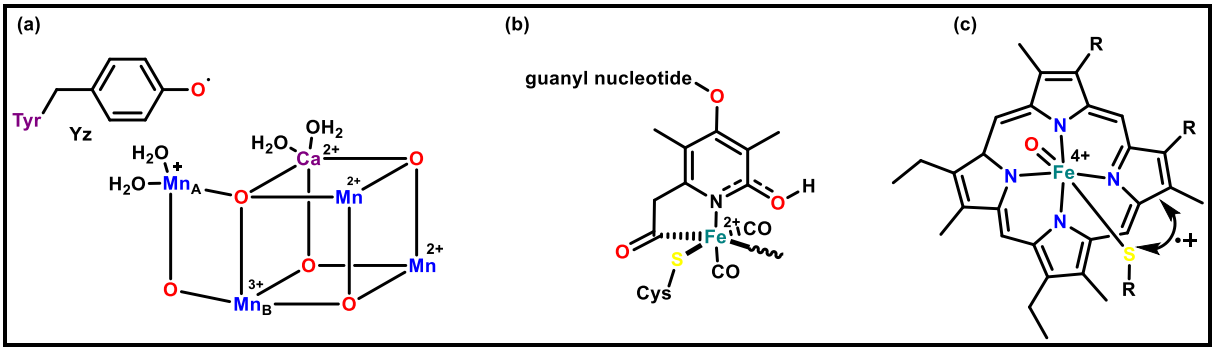


Chart 1.1 Structures of redox-active prosthetic groups present in the biologically active site of **(a)** oxygen-evolving complex in photosystem II, **(b)** iron-hydrogenase involved in H_2 transfer reactions, **(c)** oxo-ferryl intermediate present in cytochrome P450 system responsible for the oxidation of organic molecules [Praneeth et al., 2012].

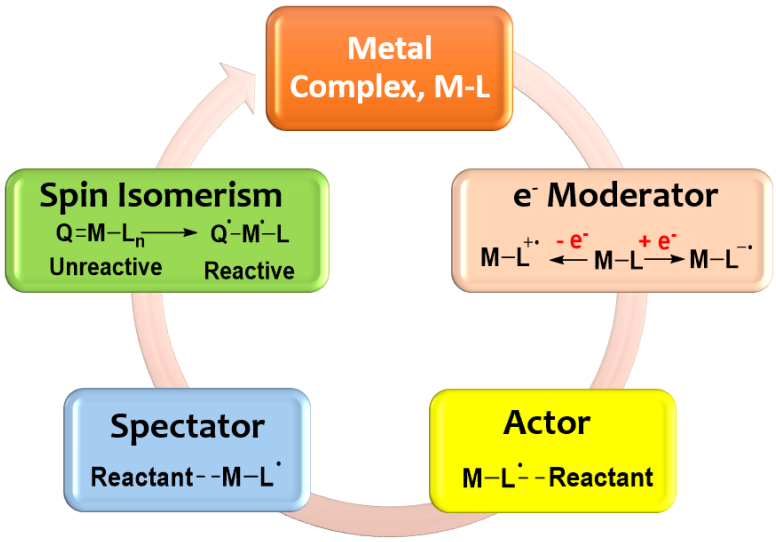


Chart 1.2 Different roles played by redox-active ligands in chemical- and electrochemical reactions [Luca et al., 2013].

1.1.1 Different Roles of Redox-active Ligands: Aiding Complex Reactions

A redox-active ligand can be an electron acceptor, donor, or radical species that can coordinate with a metal ion [Dzik et al., 2011]. Many redox-active ligand systems have been discovered in the past two decades, and many are likely to be introduced in the future. Molecular scaffolds such as catecholato, aminophenalato, benzenedithiolato, o-phenylenediamine, and phenalenyl cover a part of the wide range of redox-active ligands [Ahmed et al., 2022; Broere et al., 2015]. These ligands on metal coordination exhibit a chemically or electrochemically reversible charge-, and proton-coupled electron transfer under suitable reaction conditions. Nonetheless, there are reports where the combination of redox-active ligands with redox-active metal can even lead to ligand non-innocence. Therefore, it may be difficult to directly predict the active site or oxidation state for these systems [Ganguly et al., 2019; Jørgensen, 1966b].

Several distinctions and classifications have been made in the literature so far. Redox-active ligands can be broadly classified as [Chirik, 2011a; Kaim, 2012; Luca et al., 2013; Nakada et al., 2022]:

1. Actor ligand
2. Electron moderator
3. Spectator ligand
4. Cooperative ligand

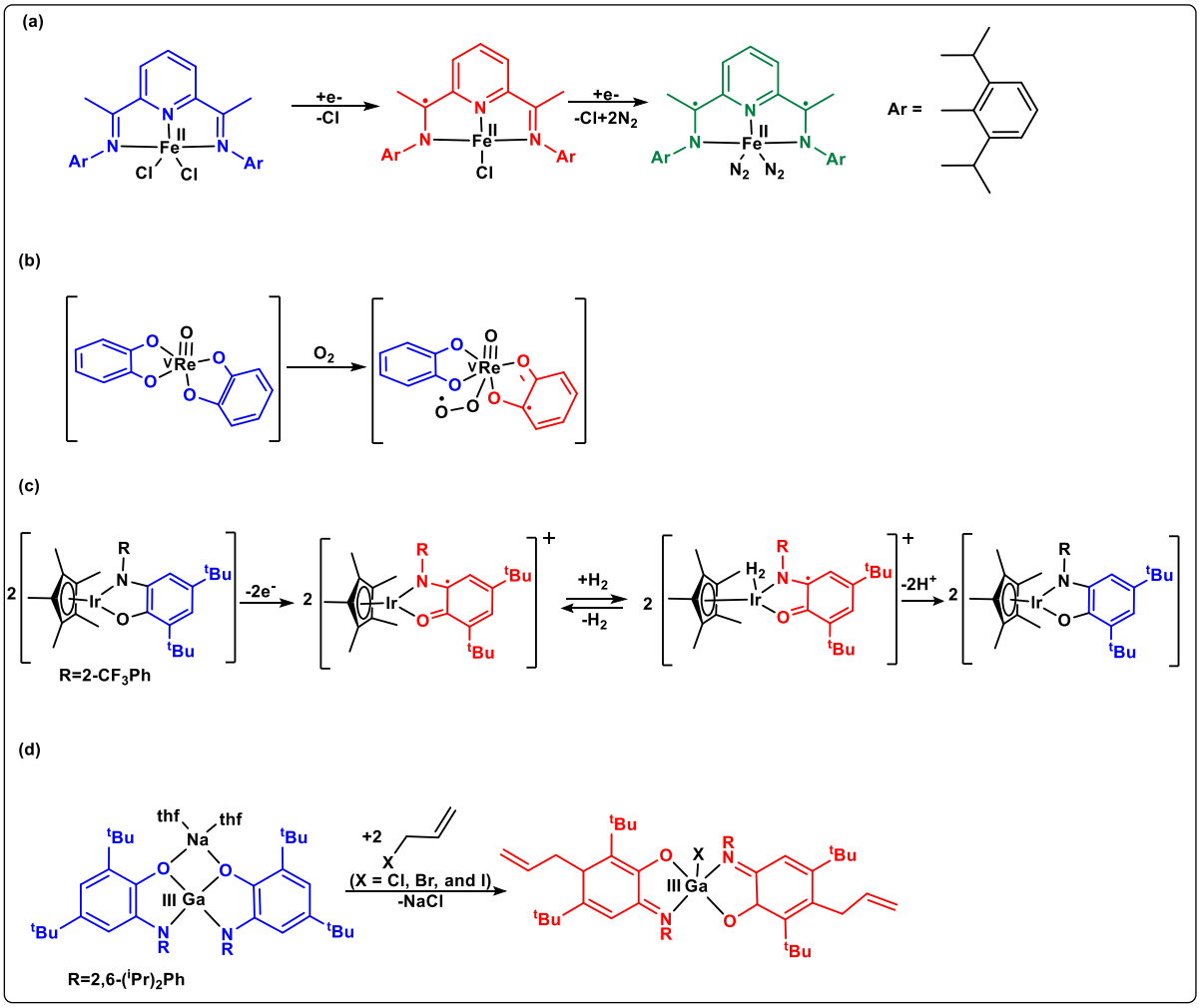


Chart 1.3 Redox-active ligand in the role of **(a)** spectator by storing charge over bis-aryliminopyridine framework in a Fe(II) complex [Bart et al., 2006]; **(b)** electron supplier for oxygen splitting by a catecholate-derived Re(V) complex [Lippert et al., 2010]; **(c)** moderator for oxidation of dihydrogen by bis-o-amidophenolate-derived Ir(II) complex [Ringenberg et al., 2008]; **(d)** activation of aryl halides in bis-o-amidophenolate-derived Ga (III) complex [Piskunov et al., 2013].

The engagement of redox active ligands directly with the substrate during any chemical reaction makes the ligand an actor in nature. For example, in the cytochrome P450 enzyme, a metal oxyl radical abstracts hydrogen atoms from the substrate [Behan et al., 2006]. Very recently, Nakada *et al.* suggested that an actor ligand can be converted to another chemical species during the reaction, which may or may not involve charge transfer from the actor ligand during the transformation [Nakada et al., 2022]. Whereas, they emphasized on the probability of a redox-active ligand to be a electron/proton supplier or pooler, when it is involved in the transfer of electrons, and protons to the substrate, or vice versa. This scenario exists when the frontier orbitals of redox-active ligand matches to that of the substrate of interest. The another possible role of a redox-active ligand is to moderate the Lewis acidity or basicity at the metal center. Mandal and co-workers has reported such Lewis acidic behavior imparted by redox-active phenalenyl ligand to a series of organoaluminium complexes [Mukherjee et al., 2013c]. Further, the plausible role of a redox-active ligand is to act as a temporary charge storage reservoir, while the coordinated metal actively participates in the chemical reaction. Such ligands are defined as spectator ligands in the literature [Luca et al., 2013]. The important classification of redox-active ligands is based on the synergic cooperation between the metal and ligand in a chemical reaction. Such ligands are cooperative ligands. They have been explored and studied intensively in the past two decades for developing bifunctional catalysts, wherein metal and ligand participate actively during substrate activation in a cooperative fashion [Gunanathan et al., 2011; Phipps et al., 2023; Rauch et al., 2020].

In general, most of the above-discussed redox-active ligands feature an organic backbone with a well-defined π-conjugated network to stabilize the extra charges. The important contribution to their redox behavior arises from the presence of interesting frontier molecular orbital (FMO) energy levels. Polycyclic odd alternant hydrocarbons (POAHs) are unique class of redox active ligands possessing both these features. The extended π-conjugated system and the availability of energetically low non-bonding molecular orbitals (NBMO) in this class of ligands have realized their applications in electric, magnetic, and photochemical domains [Mukherjee et al., 2017].

1.2 Phenalenyl(PLY): Redox-active Nanographene Fragment

Phenalenyl(PLY) is one of the redox interesting tricyclic aromatic member of the class of POAHs. POAHs are organic molecules that contain three or more aromatic hydrocarbon rings, with an odd number of carbon atoms in the π-conjugated system. They can be regarded as a fragment of an infinite nanographene sheet [Du et al., 2009]. Contrary to graphene which is a zero band gap semiconductor, POAHs due to their finite structure show a non-zero band gap [Ahmed et al., 2022; Novoselov et al., 2005]. Utilizing the linear combination of atomic orbitals (LCAO) approach for the calculation of Hu̇ckel molecular orbital, the presence of interesting non-bonding molecular orbital (NBMO) situated over π- conjugated POAHs was identified [Dewar et al., 1954; Gold et al., 1952]. The smallest POAH containing three aromatic rings and 13 carbon atoms, is named as phenalenyl(PLY) [Haddon, 1975]. Over the years, PLY has gained the peculiar attention of synthetic as well as theoretical chemists and physicists worldwide [Ahmed et al., 2022; Pal et al., 2004; Sarkar et al., 2011]. PLY moiety presents the existence in three redox forms; closed-shell cation, closed-shell anion, and open-shell radical, which can be generated on the abstraction of corresponding hydride ion, proton, and hydrogen radical from the phenalene molecule [Reid, 1965] (Chart 1.4). All the redox forms of PLY are stable and have identical symmetry elements with D_{3h} as the point group. Quantum chemical studies defined the stability of three redox states in PLY moiety, which can be attributed to the delocalization energy and gain of π-electronic energy. The PLY molecule in cationic form carries 12 π-electrons, and an empty NBMO. For the radical form, PLY has 13 π-electrons and one electron in the NBMO. The anionic PLY molecule has 14 π-electrons. Interestingly, for the PLY system, both bonding and antibonding molecular orbital wave functions contribute equally to the NBMO,

therefore the addition of electrons to NBMO does not disturb the overall bond order of the molecule. Therefore, the presence of such intriguing NBMO plays a vital role in the existence of three thermodynamically stable redox states [Chi et al., 1999; Goto et al., 1999a; Kubo, 2019; Morita et al., 2011b; Sato et al., 2007; Yang et al., 2021]. Further, these NBMO are mostly delocalized over the outer-most carbon atoms of the fused tricyclic system. The alternate carbon atoms contain the orbital lobes, while the nodal points reside on the other carbon atoms in an alternate arrangement. Such an arrangement is displayed in Chart 1.5.

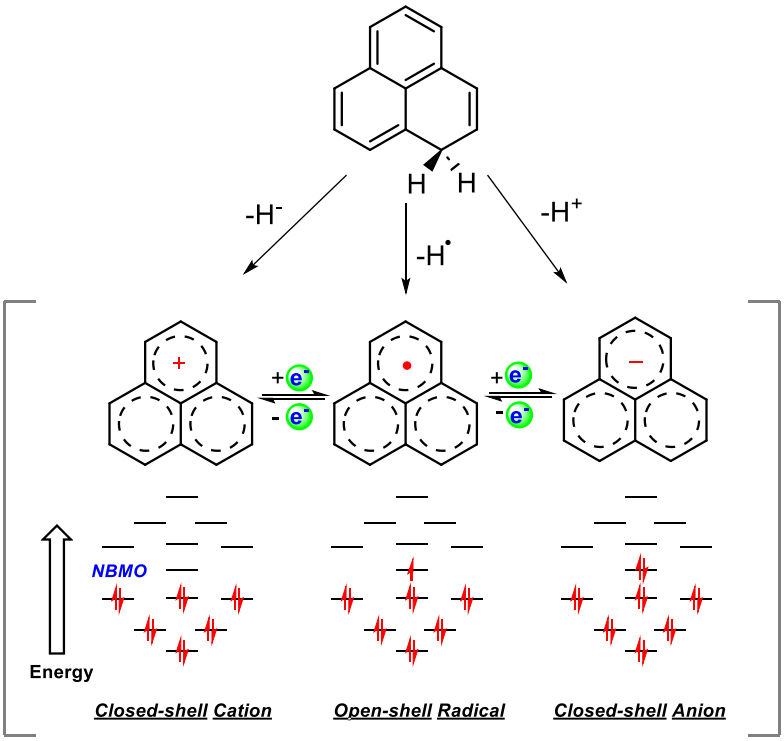


Chart 1.4 Phenalenyl (PLY) moiety in three different redox-states: closed-shell cation, open-shell radical and closed-shell anion [Ahmed et al., 2022].

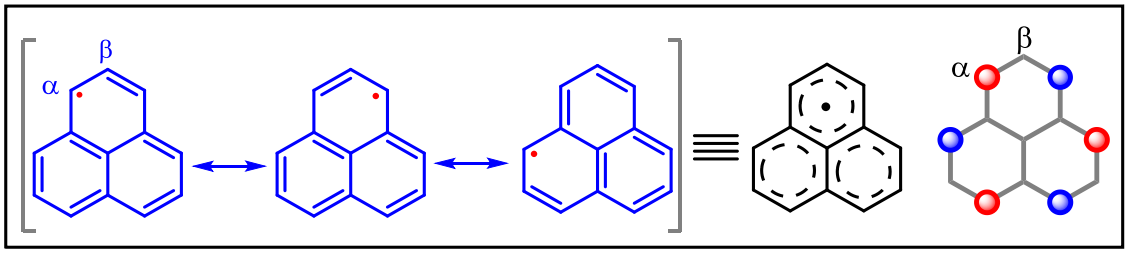


Chart 1.5 Resonating structures showing stabilization of radical over PLY scaffold, and the respective NBMO plot [Mukherjee et al., 2017].

1.2.1 Open-shell Phenalenyl: Birth of Best Organic Conductors and Challenges

Haddon [Haddon, 1975] was the first scientist to realize the importance of the PLY system. Inspired by the early Hückel calculations, he proposed the utilization of NBMO present in the PLY molecules to design radical-based single-component molecular superconductors. Further, he stated several important criteria in favor of PLY to design organic metals and superconductors. PLY is a POAH, which can take an unpaired electron in the NBMO. This unpaired electron can be the key contributor for inducing electrical conductivity. PLY molecules are gifted to have a uniform crystal structure, which allows uniform packing in the solid state, favoring uninterrupted charge transfer. Also, it was established that PLY has low ionic fluctuation energy, favoring the distribution of unpaired electrons homogeneously over the entire moiety. Therefore, the overall electron-electron repulsion is low in the solid state. The

anticipation of PLY-based radicals for adopting π-π stacking interactions allowed substantial overlap of conducting molecular orbitals (CMOs), as they do not contain any counterion in the crystal lattice (Chart 1.6a). These characteristics prompted the application of PLY-based radicals in solid-state conductors. Nevertheless, the initial efforts to isolate PLY in the radical form failed, as the result of dimerization by σ- and π- association in the PLY radicals. Nakasuji's group developed a six-stage amphoterically redox-active compound by combining three PLY units [Kubo et al., 1996]. Later, Yamamoto and Nakasuji successfully reported the first radical on a PLY scaffold containing the bulky *tert*-butyl groups [Goto et al., 1999b]. Another stable PLY radical containing *tri-tert*-butyl groups was developed by Morita, Takui, and coworkers, which was used as electroactive material in secondary batteries [Morita et al., 2011a]. Kubo and Kertesz reported the stacking in PLY radicals supported by non-classical multicentre bonds [Mou et al., 2014]. Meanwhile, Haddon's group paved the way for developing molecules featuring extended conjugation by connecting PLY units through a central atom [Mandal et al., 2006]. Such an approach led to the development of best-performing molecular conductors [Morita et al., 2011b]. These molecular designs exhibited molecular bistability in three of the physical channels (electric, magnetic, and optical domains) [Hicks, 2011b]. However, these tremendous efforts were challenged due to the limitations in producing stable PLY radicals for practical applications [Kubo, 2015].

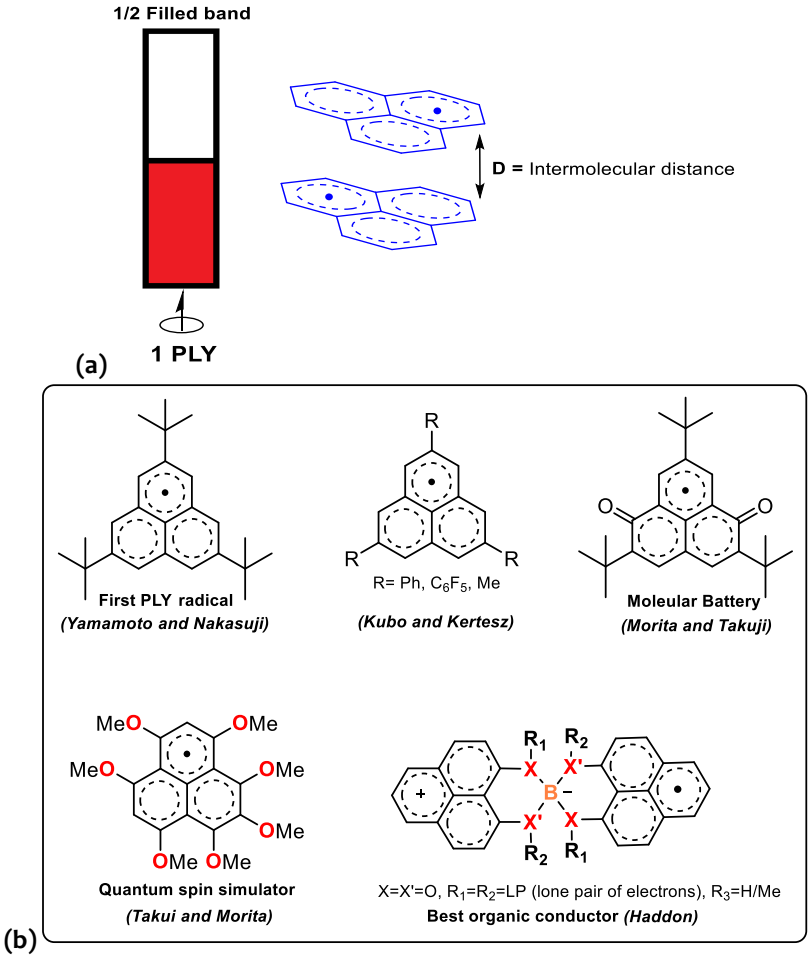


Chart 1.6 (a) Pictorial representation for the conceptual use of PLY-derived radicals in organic conductors [Ahmed et al., 2022; Chi et al., 2002]. **(b)** Selected examples of stable PLY-based radicals [Mukherjee et al., 2017].

1.2.2 Closed-shell Phenalenyl: Important Convention to Develop Stable PLY Radicals

Despite the previous challenges encountered in developing stable PLY radicals by various research groups, Mandal and co-workers introduced an alternative approach for developing

stable PLY radicals. They postulated an approach where the closed-shell cationic state of PLY can be used to generate an open-shell radical state [Mukherjee et al., 2017]. Since, the cationic state of PLY contains electronically accessible NBMO, which can readily accept electrons on external spin injection to generate in-situ stable PLY radicals. Such a design circumvents the challenges earlier faced for developing stable open-shell radical states directly from PLY precursors.

1.3 Closed-shell Phenalenyl-based Metal Complexes: A Coordination Chemistry Approach

The coordination of PLY-based ligands to a metal ion is known to generate a closed-shell cationic state of PLY. Such an illustration of PLY with a trivalent metal ion, suggested by Mandal and co-workers is shown in Chart 1.7. Similar resonating structures for spiro-conjugated boron-PLY compounds were employed by Haddon and co-workers. The positive charge in these structures (Chart 1.7), is assigned to the PLY rings, and the negative charge was given to the coordinated atom. With this novel approach, a variety of PLY ligands, containing O, and N- atoms as coordinating sites were prepared. *9-hydroxy-1H-phenalen-1-one* (L1, Chart 1.8*)* is the smallest PLY-based ligand and an important organic precursor for preparing other derivatives of PLY. *9-hydroxy-1H-phenalen-1-one* contains β-hydroxyketone type functional group that has a similar chelating coordinating properties as the one present in 2,4-pentanedione (acac). The ligand strength of L1 is further enhanced by following the organic functionalization proposed by Franz and Martin [Franz et al., 1978], introducing N- atoms as coordinating sites in ligands, L2-L5. Nevertheless, very recently our research group has introduced the PLY molecule to the class of Schiff-base ligands using an alternative approach, which is discussed in Chapter 5 of the thesis. Ligands, L1-L5 have been used to design metal complexes, which have found intriguing applications in the domain of memory storage devices and catalysis.

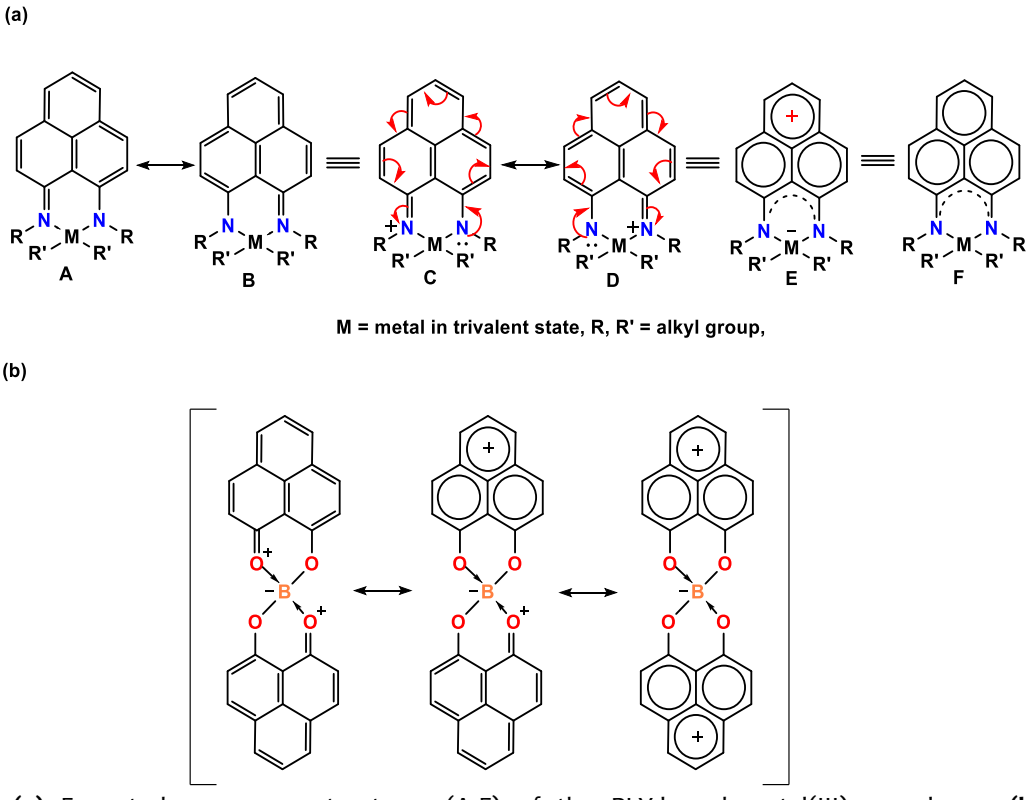


Chart 1.7 (a) Expected resonance structures (A-F) of the PLY-based metal(III) complexes. **(b)** Charge delocalization in Haddon's spiro-biphenylene boron compounds [Mukherjee et al., 2017].

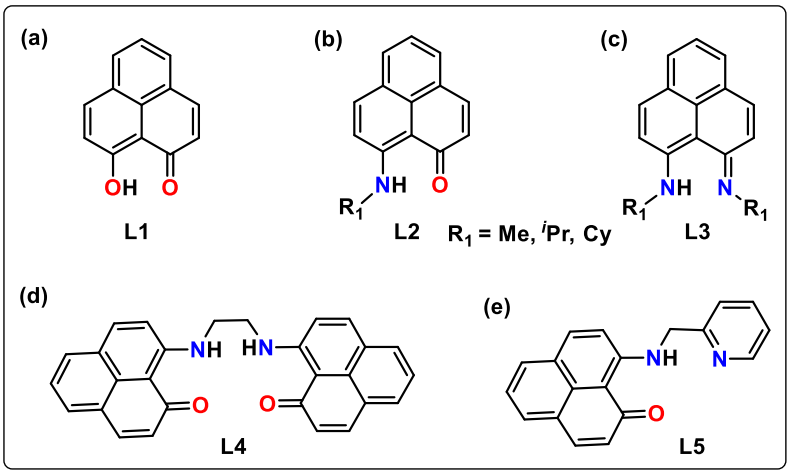


Chart 1.8 Representative examples of organic ligands explored for generating closed-shell cationic PLY state on metal complexation [Bhunia et al., 2019a; Chakraborty et al., 2020a; Das et al., 2019b; Kamboj et al., 2022, 2023a; Vijaykumar et al., 2019; Wahl et al., 2019a].

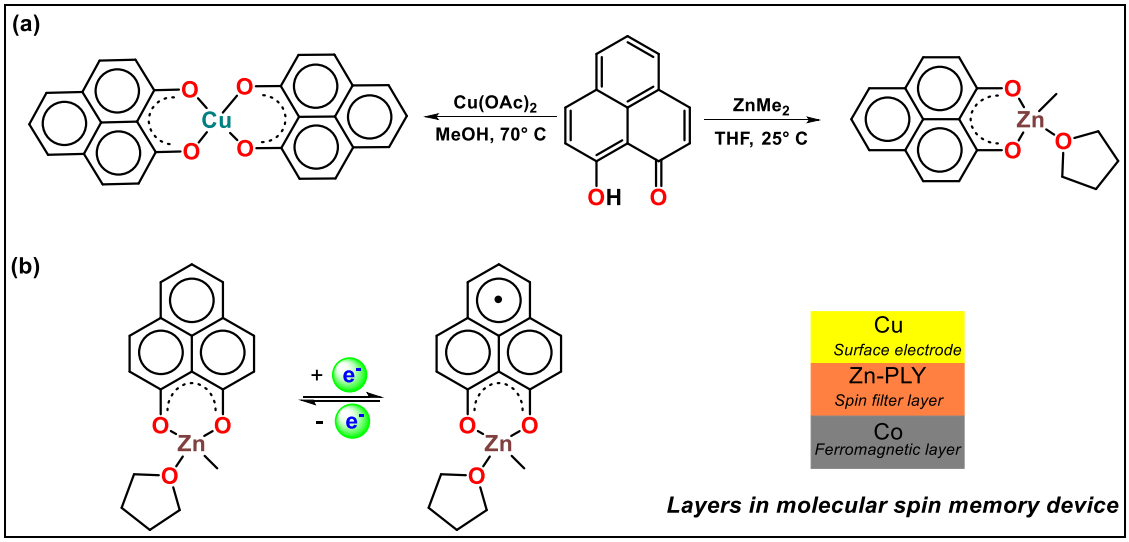
1.3.1 Closed-shell Phenalenyl in Spin- (Spintronics) and Resistive Memory Devices: Next-generation Data Storage Devices

Early literature in PLY radical chemistry was primarily focused on their synthesis, stabilization, and crystallization. Later, with the help of analytical characterization tools, such as single crystal X-ray diffraction (SCXRD) technique and electron paramagnetic resonance (EPR) spectroscopy, etc., the radicals were structurally characterized and efforts were made to understand their molecular orbitals. Such understanding has led to the pursuit of exploring the electric, magnetic, and electrochemical behavior of PLY radicals in solid- and solution-state. Utilizing the approach suggested by Mandal and co-workers, in-situ generation of PLY radicals on metal coordination to L1 was explored for spin memory devices. These devices are data storage devices that store non-volatile memory based on electronic spins, and are one of the promising data storage devices for offering high-performance, and high-density memories [Koplovitz et al., 2017].

- **Spin Memory Devices Based on Organozinc(II) and Copper(II) Phenalenyl Complexes**

Moodera and co-workers prepared an organozinc complex with PLY ligand, L1 (Scheme 1.1) [Raman et al., 2013]. It was used to fabricate a spin memory device with copper as top electrode and cobalt as the bottom ferromagnetic contact electrode. The evaluation of the magneto-transport behavior of the fabricated device displayed resistance which was spin-dependent, leading to an interfacial magnetoresistance. Switching the cobalt magnetization to coercive field developed a magnetoresistance signal of the order >20%. The unprecedented behaviour of the device was explained with spin-filtration mechanism. The ability of Zn(II)-PLY complex to accept electronic spin in the NBMO from the ferromagnetic cobalt layer contributed to the spin-filtration mechanism. Detailed DFT studies confirmed the spin-transfer from the d-orbitals (d_{z^2}, d_{xz} and d_{yz}) of cobalt to the first molecular layer via the p_z-orbitals of PLY ligand. The planar structure of Zn(II)-PLY complex allowed uninterrupted spin transfer. The PLY ring of first molecule developed a partial radical character, and acted as a donor layer. The interaction of this donor layer with the second layer that behaved as an acceptor, led to the formation of donor-acceptor type pi-dimer with ~3.26 Å interlayer separation (smaller than van der Waals radii between carbon atoms). Computational studies suggested the spin-split in Fermi energy (LUMO) level (~0.14 eV), responsible for the spin-filtration behaviour, giving an unprecedented magneto resistance behaviour. Very recently Münzenberg and co-workers developed another planar complex using the previously employed L1 ligand [Jha et al., 2023]. The synthesis of

Cu(II)-PLY complex is shown in Scheme 1.1. The device was fabricated with copper/cobalt as the top contact electrode and cobalt as the bottom ferromagnetic electrode. A mechanism similar to the one for Zn(II)-PLY complex was established and the important contribution of NBMO situated over the PLY backbone was realized.



Scheme 1.1 (a) Synthesis of Zn(II)-PLY [Raman et al., 2013] and Cu(II)-PLY [Jha et al., 2023] complexes employed as active materials in spin memory device. **(b)** Spin injection to NBMO of Zn(II)-PLY complex from the ferromagnetic bottom Co layer in the constructed spin memory device.

- **Introducing Closed-shell Phenalenyl to the Domain of Resistive Memory Devices**

  PLY-based molecules have been employed in designing conductors, secondary batteries, and spin memory devices. Also, the planar geometry in these molecules served an important role in developing important charge-transfer processes through the NBMO. Very recently, our research group has introduced PLY to the field of resistive memory devices. Resistive memory, often called resistive random-access memory (ReRAM or RRAM) is one of the propitious candidates for next-generation data storage in electronic devices. Changing the resistance under an applied electric field across a solid-state material can store data in a non-volatile manner, giving rise to the RRAM behavior. Chapter 3 of the thesis covers the synthesis and utilization of a planar Co(II)-based complex, [Co^{II}L], derived from a L4 ligand as an active material for an RRAM device [Kamboj et al., 2023a].

1.3.2 Closed-shell Phenalenyl in Catalysis: Mimicking Noble Metal Behavior

The sections discussed above so far have highlighted the potential of PLY to mimic metal-like behavior, such as electron transport, bistability in molecular states, spin-filtration, etc. The unique molecular orbitals, NBMO, in PLY-based molecules, have found tremendous applications in material science. Mandal and co-workers introduced PLY scaffold to the field of catalysis. They have foreseen the possibility of PLY-based metal catalysts to conduct organic transformations, which are otherwise difficult to conduct with main group and base metal complexes. PLY-based molecules support the chemical transformation in three different ways:

(1) Imparting Lewis acidity
(2) Spectator ligand
(3) Redox catalysis: Actor/co-operator/moderator.

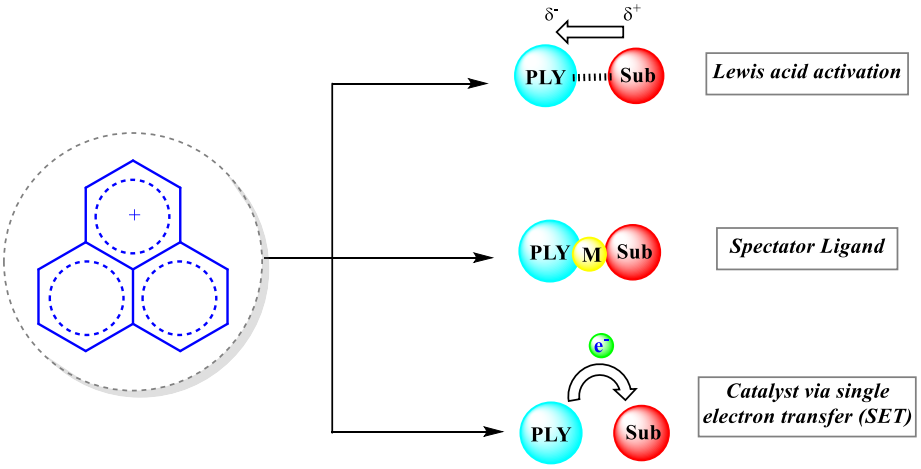
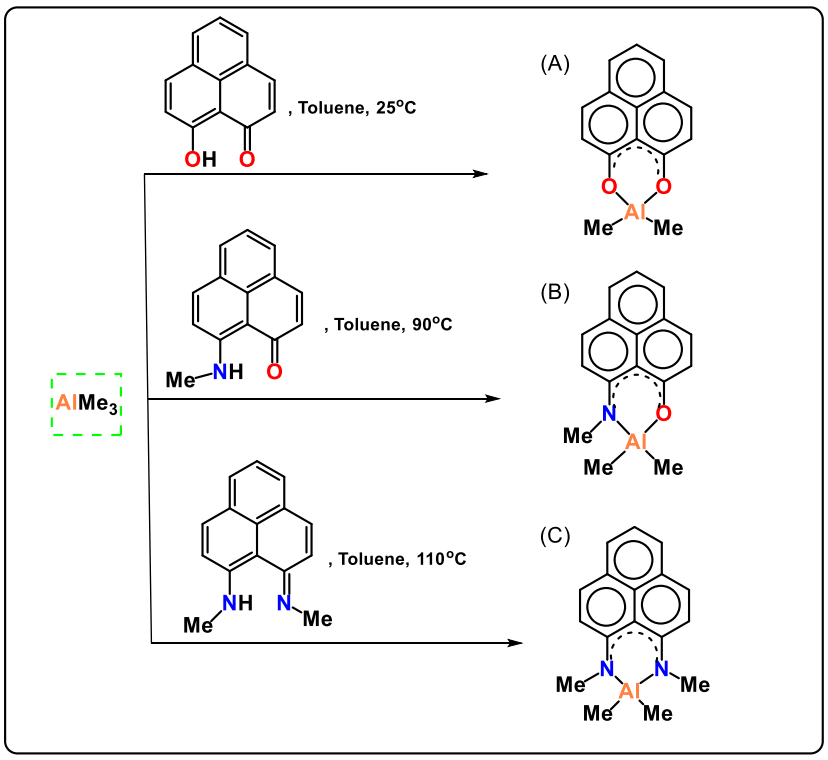


Chart 1.9 Different types of PLY-mediated catalysis [Ahmed et al., 2022].

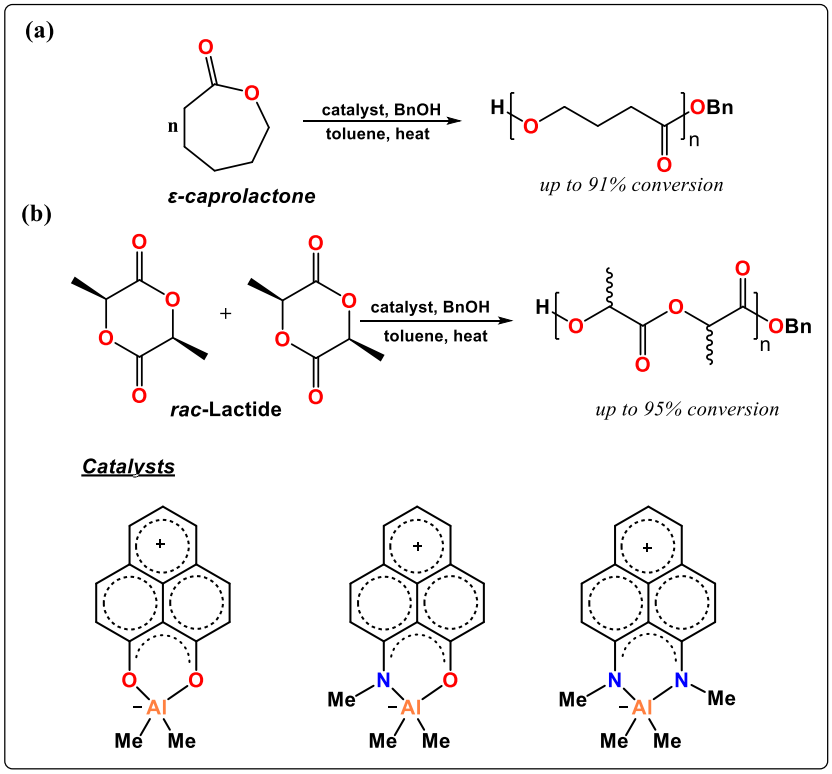
1.3.2.1 Phenalenyl-induced Lewis-acid Catalysis



Scheme 1.2 Schematic preparation of Al(III)-PLY complexes [Sen et al., 2012] with L1, L2, and L3 type ligands.

The existence of energetically accessible LUMO, which is NBMO in the case of PLY, can be advantageous to design molecules that can perform Lewis acid-catalyzed organic transformations. As discussed in the previous section, such orbitals are readily available in cationic-closed shell PLY, which can be generated easily on metal coordination. Another approach suggested was the alkylation of 1,9-heteroatom substituted PLY molecules, on the treatment with reagents such as Meerwin salt containing the electrophilic alkyl groups [Franz et al., 1978; Haddon et al., 1981]. Both the approaches successfully created electron deficiency on the PLY moiety, which caused Lewis acid-type interactions between the PLY and substrate under study. Mandal and co-workers employed the coordination of PLY ligands, L1, L2, and L3 to effectively obtain a series of Al(III)-PLY complexes with enhanced Lewis acidity. Such an enhanced Lewis acid characteristics in the Al(III)-PLY complexes lead to the successful catalytic

ring-opening polymerization of cyclic esters, ε-caprolactone (ε-CL) and lactide (LA), giving a yield above 90% of the respective products [Sen et al., 2012] (Scheme 1.2 and 1.3).



Scheme 1.3 The catalytic activity of Al(III)-PLY complexes for ring-opening polymerization of cyclic esters, ε-caprolactone (ε-CL), and lactide (LA) [Sen et al., 2012].

1.3.2.2 Phenalenyl in the Role of a Spectator

- **Catalysing Hydroamination Reaction**

The role of PLY as a spectator was realized while performing catalytic hydroamination of carbodiimides with p-toluidine, utilizing a series of Al(III)-PLY as catalyst (Scheme 1.4). This reaction yielded N, N′, N′-trisubstituted guanidine in 98% yield as the product. Mechanistic investigations revealed the activation of the substrate took place at the metal center [Mukherjee et al., 2013c]. Later, a series of organozinc (II)-PLY complexes were used for the catalytic alkene hydroamination reaction [Mukherjee et al., 2013b]. This reaction facilitated the introduction of the N-H bond of amine to the unsaturated C-C bonds of alkenes.

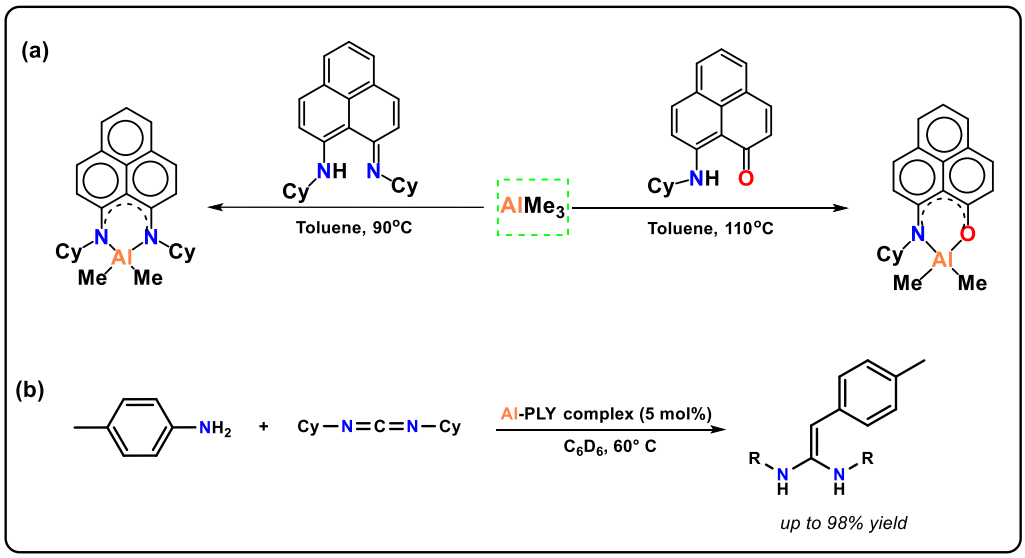
- **Facilitating Reduction of Substrates with Silanes**

Fe(III) and Mn(II) complexes, with PLY-based ligand L4, were used for catalytic reductions of nitrides and amides (Scheme 1.5). In literature, such reactions are generally performed with lithium or sodium aluminum hydride as the reducing agent under harsh conditions. Even hydrogenation with Pd/C is also an ineffective process for these conversions. The Fe-PLY complex catalyzed the reduction of the nitrile group to amine, giving up to 98% yield, with polymethylhydrosiloxane (PHMS) as a reducing agent [Das et al., 2019b]. Another Mn-PLY complex catalyzed the reduction of prime amide groups in the presence of phenylsilane as a reducing agent, with a 95% yield [Das et al., 2019a]. Both these reactions were primarily metal-facilitated, and PLY played the role of a spectator ligand.

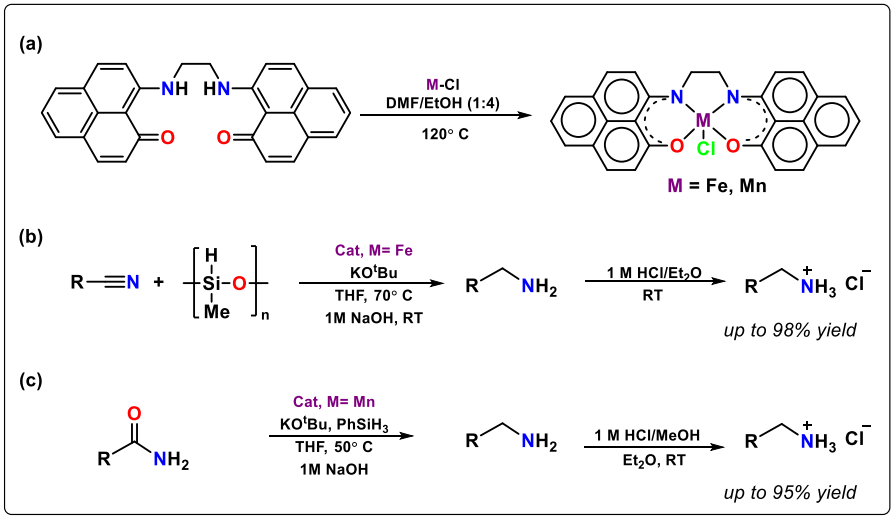
- **Oxidation of Polycyclic Aromatic Hydrocarbons (PAHs)**

Our research group has investigated the role of a PLY-based Cu(II) complex, [Cu^{II}L], with a similar ligand (L4) for the oxidation of PAHs. PAHs such as naphthalene,

anthracene, pyrene, etc can harm the environment in the form of frequent industrial waste. Oxidation of these toxic hydrocarbons can be a suggested route for their detoxification. Moreover, the oxidation products such as quinones and pyrenol are important molecules in the drug industry. However, these transformations are generally favored by Ru and Pd catalysts. In our approach, PLY-derived ligand L4 in coordination with Cu(II) metal has facilitated these conversions in good yields. The detailed synthesis and catalytic activity of the complex are discussed in Chapter 4 [Kamboj et al., 2022].



Scheme 1.4 (a) Synthetic procedure for preparing Al-PLY complexes, **(b)** their catalytic activity in carbodiimides hydroamination reaction [Mukherjee et al., 2013c].



Scheme 1.5 (a) Synthetic procedure for preparing Fe/Mn(III)-PLY complexes, **(b)** their catalytic activity in the reduction of nitriles, and **(d)** amide functional groups [Das et al., 2019a, 2019b].

- **Electrocatalytic Oxygen Evolution Reaction (OER)**
  So far, the role of PLY as a spectator ligand has been identified for various organic catalytic transformations. Our research group has utilized the PLY-based ligand (*9-(2-(3,6-di-tertbutyl-2-hydroxybenzylidene)hydrazineyl)-1H-phenalen-1-one*, dtbh-PLYH_2) coordination to generate a dinuclear Ni(II) complex, [Ni^{II}(dtbh-PLY)$_2$]. Chapter 6 of this thesis covers the detailed studies of dinuclear Ni(II) complex, where it is employed as an electrocatalyst for the oxygen evolution reaction (OER). This is the first report where an OER study is conducted with electrocatalyst based on the phenalenyl-derived metal complex.

1.3.2.3 Phenalenyl as a Redox Catalyst

The common feature of redox-active ligands is the distinguished ability to behave as an electron reservoir that can impart exceptional behavior in the respective metal complexes. Also, it is well established that most of the catalytic cycles involve multi-electron transfer processes. For instance, oxidation addition reactions and reductive elimination reactions are facilitated by at least two electron transfer mechanisms. Most of these transformations are catalyzed by noble metals, such as Rh, Pt, Pd, etc. Similar activity is less pronounced for catalysts based on first-row transition metals. Therefore, as per the proposal given by Wieghardt and Chirik, combining a redox-active ligand with first-row transition metal can mimic noble metals' activity during catalytic cycles. Mandal and co-workers utilized this strategy judiciously to employ PLY-based metal complexes as redox reservoirs to achieve organic transformations, which were otherwise well-known with noble metals previously.

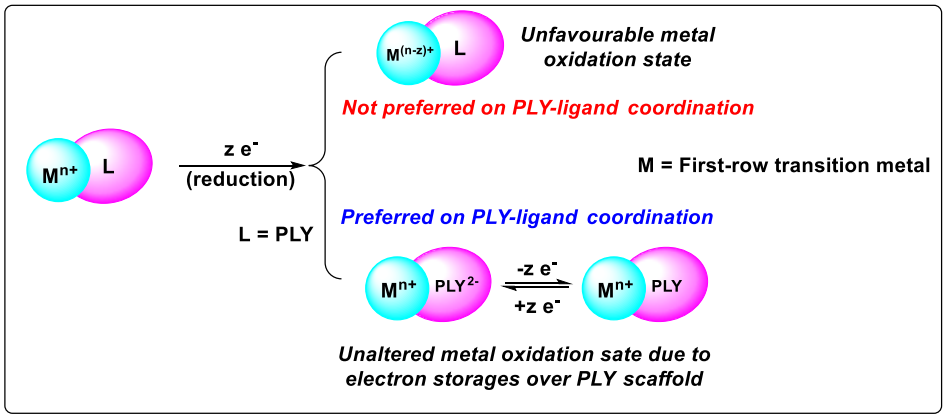
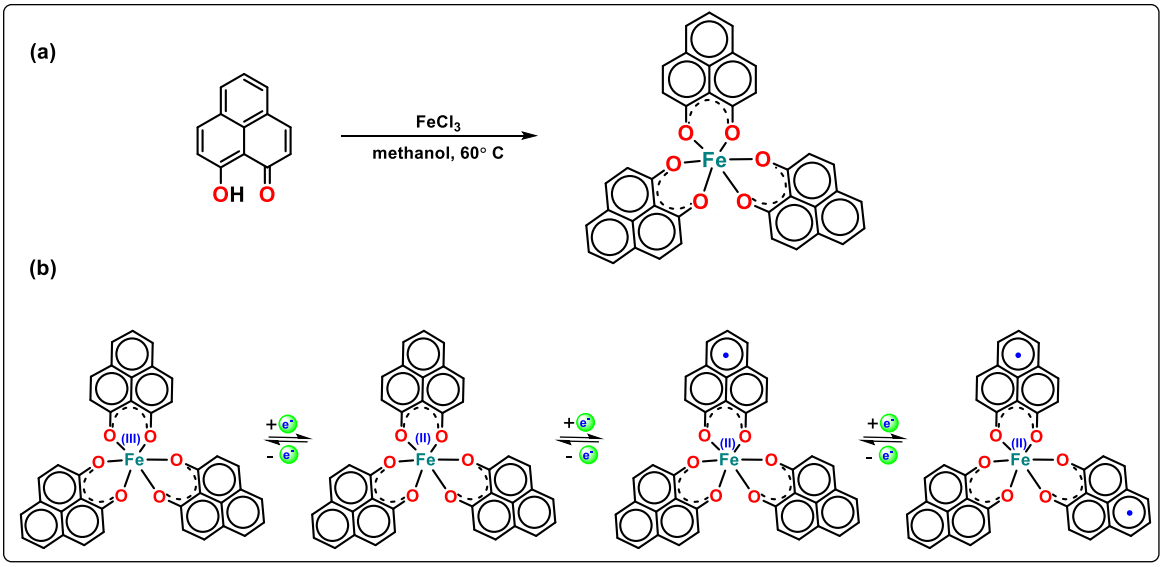


Chart 1.10 Role of PLY in designing redox catalysts using first-row transition metals [Ahmed et al., 2022].



Scheme 1.6 (a) Synthetic procedure for preparing Fe(III)-PLY complex, and **(b)** the observed redox characteristics [Pariyar et al., 2015].

- **Iron(III)-Phenalenyl Complex as a Cathode for H_2O_2 Reduction**

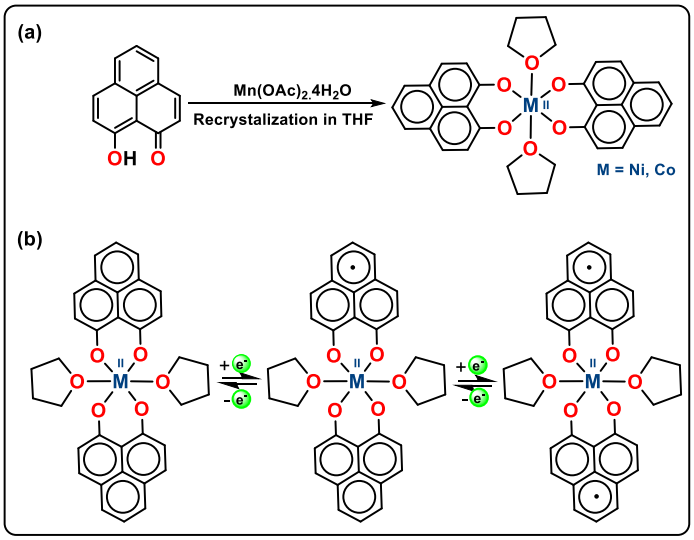
The H_2O_2 fuel cell has been regarded as a clean energy source, with a theoretical output of 1.09 V, giving benign H_2O and O_2 as the byproducts. A Fe(III) complex containing PLY coordination of L1 ligand, $Fe(PLY)_3$ was prepared by Mandal and coworkers, and employed as a cathode material for H_2O_2 reduction in H_2O_2 fuel cells (Scheme 1.6). For the operation of the fuel cell, the reaction at the anode generates electrons, which are transferred to the cathode surface, containing $Fe(PLY)_3$ complex. The first reduction leads to an oxidation state

of Fe from +3 to +2 and the following next two reductions were PLY cantered. The H_2O_2 fuel cell designed with $Fe(PLY)_3$ complex as cathode, and Ni foam anode showed an open circuit potential (OCP) of 0.74 V, and a peak power density (PPD) of 1.43 mW cm^{-2}. From the cyclic voltammetric (CV) and DFT studies, the role of PLY in reducing additional H_2O_2 molecules was explained.

A new synthetic strategy designed by our group (Chapter 5) has been judiciously utilized to prepare novel PLY-based dinuclear transition metal complexes. The dinuclear Fe(III) complexes prepared with this strategy, $[Fe_2(hmbh\text{-}PLY)_3]$ and $[Fe_2(hnmh\text{-}PLY)_3]$ (hmbh-$PLYH_2$ = *9-(2-(2-hydroxy-3-methoxybenzylidene)hydrazineyl)-1H-phenalen-1-one* and hnmh-$PLYH_2$ = *9-(2-((2-hydroxynaphthalen-1-yl)methylene)hydrazineyl)-1H-phenalen-1-one*), has been employed as a cathode material for H_2O_2 reduction. As a consequence of additional Fe(III) center in these dinuclear complexes, very high PPD values (2.43 and 2.84 mW cm^{-2}) were obtained. The details are discussed in Chapter 5 of the thesis.

- **Activation of B-H/Si-H Bonds and Functionalization**

Hydroboration and hydrosilylation of alkene or alkyne functional groups can lead to the corresponding hydroborylated and hydrosilylated derivatives, which are important substrates for industrial applications. The former conversion is popularly catalyzed by a Ru-based catalyst, whereas the latter conversion requires a Pt-based catalyst. PLY coordination (through the L1 ligand) to the Ni(II) metal ion in $Ni(PLY)_2$ complex facilitated these transformations. Besides, the CV and DFT studies suggested the presence of PLY-based LUMO orbitals in the $Ni(PLY)_2$ complex. Therefore, PLY could behave as an electron reservoir, and house electrons on external spin injection (Scheme 1.7). The $Ni(PLY)_2$ complex catalyzed hydrosilylation and hydroboration reactions, with a 90% yield of the desired products. Later, a similarly designed Co(II) complex, $Co(PLY)_2$ was prepared and displayed a similar molecular organization, where the LUMO was predominately PLY cantered (Scheme 1.7). $Co(PLY)_2$ catalyzed the reduction of carboxylic acid in the presence of silane as the reducing agent.



Scheme 1.7 (a) Synthetic procedure for preparing complexes $M(PLY)_2$, M = Co, Ni ; and **(b)** the observed redox characteristics [Bhunia et al., 2019a; Vijaykumar et al., 2018].

1.4 Scope of the Thesis

The sections discussed above explain the significance of PLY containing metal complexes in designing solid-state devices and catalysis. The present thesis covers the novel synthetic aspects of designing PLY-based ligands, their complexes with first-row transition metal ions (Co, Cu,

Fe, and Ni) and explored their redox chemistry for several applications, such as resistive memory device and electrocatalysis. Moreover, the role of PLY as a spectator, and redox catalyst has been identified. The order of the elaborated discussion on various closed-shell phenalenyl complexes in this thesis is described below:

- Mononuclear complexes with PLY-based ligand, LH_2 = *9,9´-(ethane-1,2-diylbis(azanediyl))bis(1H-phenalen-1-one)*:

1. A square-planar [$Co^{II}L$] complex, **1** containing a tetradentate PLY-based ligand (LH_2) is prepared and structurally characterized by a set of characterization tools, including the SCXRD technique. The Co(II) complex is further employed as an active material in resistive memory device.
2. A square-planar [$Cu^{II}L$] complex, **2** containing a tetradentate PLY-based ligand, LH_2 is prepared, and structurally characterized. The Cu(II) complex is used as a catalyst for the oxidation of PAHs.

- Introducing a new PLY precursor, *9-hydrazineyl-1H-phenalen-1-one* (Hz-PLY) to prepare ligands, *(E)-9-(2-(2-hydroxy-3-methoxybenzylidene)hydrazineyl)-1H-phenalen-1-one* (hmbh-$PLYH_2$), *(E)-9-(2-((2-hydroxynaphthalen-1-yl)methylene)hydrazineyl)-1H-phenalen-1-one* (hnmh-$PLYH_2$), and *9-(2-(3,6-di-tert-butyl-2-hydroxybenzylidene)hydrazineyl)-1H-phenalen-1-one* (dtbh-$PLYH_2$) for synthesizing dinuclear metal complexes.

3. Dinuclear Fe(III) complexes, [Fe_2(hmbh-$PLY)_3$], **3** and [Fe_2(hnmh-$PLY)_3$] **4**, with PLY-based ligands, hmbh-$PLYH_2$, and hnmh-$PLYH_2$ are synthesized, and extensively characterized by a set of characterization tools, including SCXRD technique. Both the complexes are employed as a cathode for the electrocatalytic reduction of H_2O_2 in an one-compartment H_2O_2 fuel cell.
4. A dinuclear Ni(II) complex, [Ni_2(dtbh-$PLY)_2$], **5** was prepared with dtbh-$PLYH_2$ ligand and structurally characterized. It has been employed as an electrocatalyst for oxygen evolution reaction in an aqueous 1.0 M KOH solution.

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