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Synthesis, electrical conductivity and NIR absorption of some metal dithiolene complexes: some recent developments

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Square planar transition metal bis(dithiolene) complexes are of upsurge interest throughout the last few decades due to their varied interesting physical as well as physicochemical properties. Random studies on design and synthesis of semiconducting materials based on metal dithiolene complexes are going on. Moreover, shift at intense Near Infrared (NIR) region, high electrical conductivity, non-linear optical activity, electrochemical behaviours etc. are some of its interesting activities. It is important to note that a minute tailoring in its ligand backbone (which results change in its electron delocalization) results in appreciable amount of variation in its physicochemical behaviour. In this present endeavour, research works on synthesis, solid-state electrical conductivity and NIR absorption studies of square planar transition metal dithiolene complexes from near past to present days have been discussed with survey of recent work and its futuristic applications so far.

Keywords: Dithiolene, Electrical conductor, Semiconductor, Near Infrared (NIR) absorption

Design and synthesis of metal dithiolenes complexes are the subject of growing interest in coordination chemistry because of its varied solid-state properties which include electrical conductivity, non-linear optical (NLO) activity, absorption of Near Infra Red (NIR) radiation, electrochemical behaviour, etc. The *dithiolenes* having an *ene* and two *thiol* groups in its basic backbone are of those few ligands which are extremely difficult to isolate in its free state. The ligands (dithiolenes) favourably complexed with the metal ions in square planar geometry generally allow the delocalization of its loosely bound π electrons resulting various electronic as well as optoelectronic properties and it is needless to say that dithiolenes are redox active ligands. Investigation on chemistry of dithiolenes was initiated by Schrauzer, Gray and Holm in the early 1960s [1], though the term *dithiolene* was first coined by McCleverty and Balch in 1968 [1]. As stated earlier, dithiolenes are unsaturated bidentate ligands containing two sulfur donor centers which ligate to the metal ion (Fig. 1, where $R_1 = R_2$ or $R_1 \neq R_2$ and M = metal ions) to form the complex. Group 10 metal ions of Periodic Table [Ni(II), Pd(II), Pt(II)] having their favorable d^8 valence shell electronic configurations to adopt square planar geometry are good choice for metal dithiolene complexes.

The synthesis of dithiolene ligand based metal complexes is a complicated one. Early research on this field was restricted to only its synthesis, structure and reactivity. Optimum researches on this field from near past to recent days have exposed the different electronic, optoelectronic and biological properties [2] of dithiolene ligand based metal complexes like NIR absorption [3,4], NLO activity[5-13], electrical conductivity [14-16,38, 39], electrochemical property [17,18], different biological activity (bio-catalytic activities, mimicking active sites of enzymes, etc.) [19-23], etc. Later, keenness on this field was further weighed by electrochemical synthesis of metal dithiolene complexes as organic-inorganic hybrid materials with perylene as the organic part [24]. It appeared clear that modification of the ligand structure has a great influence on the solid-state as well as optical properties of this type of complex, which often finds it as a good candidate to be used in organic electronics and opto-electronics. From the very initiation, a huge varieties of 1,2-dithiolate derivatives have been reported. A few

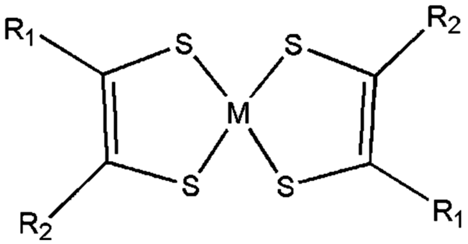


Fig. 1 — Metal bis(dithiolene) complex

of them are schematically represented in Fig. 2 [31,41,42,55,74].

Among these previously reported dithiolenes, the mnt^{2-} has been studied quite extensively for the new search of metal dithiolene based semiconductor. Also at the same time benzenehexathiol (BHT), benzenetetrathiol (BTT) based conducting metal dithiolene coordination polymers have been reported so far.

Metal dithiolene complexes have been investigated since last few decades of previous century. The major importance of synthesizing this complex lies in its unique physicochemical properties which are supposed to be applied for various futuristic applications based on its electrical conductivity (by the preparation of dithiolene based semiconductor), NIR dyes and Q-switch laser dyes, catalysis and bioinorganic studies, etc.

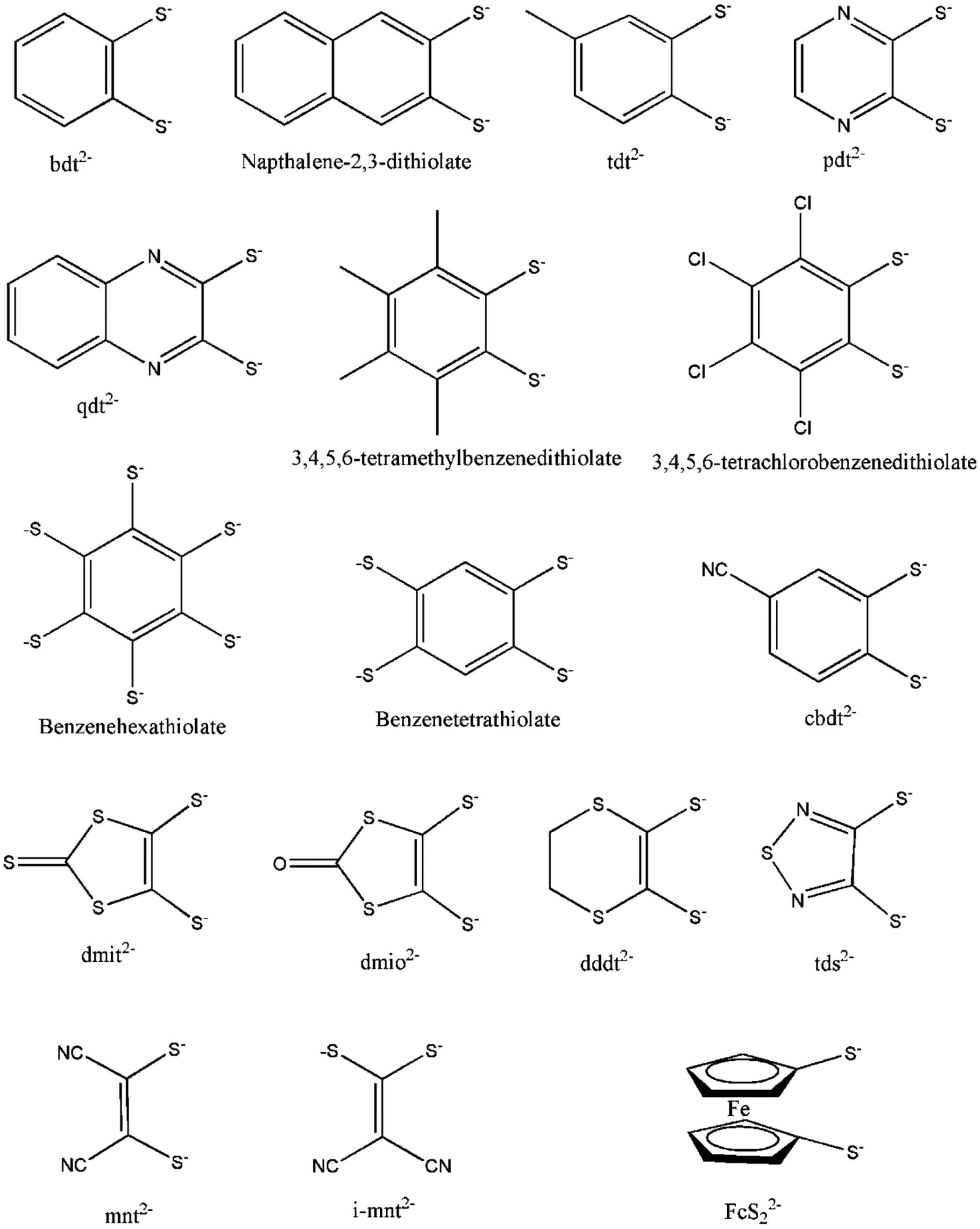


Fig. 2 — A few varieties of 1,2-dithiolate derivatives[31, 41, 42, 55, 74]

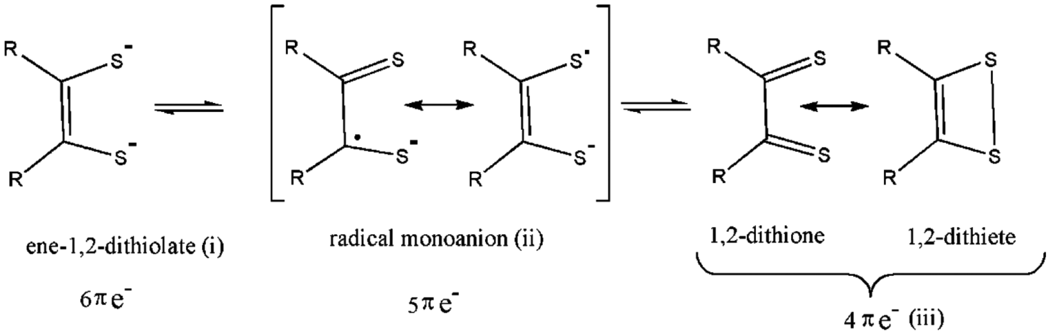


Fig. 3 — Different forms of redox active non-innocent dithiolene ligand[77, 78]

Present review emphasizes on the structure, bonding, chemical synthesis and few of chemical properties (electrical conductivity and near infrared absorption) of square planar transition metal bis(dithiolene) complexes. Due to its unique physical as well as chemical properties, it might be expected to develop some new class of metal dithiolene complexes appropriate to be used in photoelectric research.

Bonding and classification of metal dithiolene complexes

Dithiolene ligands are non-innocent redox active. Both the free dithiolene ligand and its metal complexes can exhibit different extent of oxidation states (Fig. 3). The bonding description with respect of FMO (Frontier molecular Orbital) approach with electron occupancy for the free dithiolene ligand is quite interesting and can be depicted as Fig. 4. Such bonding descriptions are judged by careful measurement (with X-ray diffraction study) of various C-C and C-S bond distances[78]. Generally, increment of electron density around a particular bond results in shortening of the bond length. So, it is expected that in ene-1,2-dithiolate form the C-S bond distance will be longest (about 1.76 Å) as it contains single bond character; whereas in radical monoanionic form the C-S bond distance reduces to 1.71 Å and remains lowest in 1,2-dithione form (about 1.68 Å), as it contains double bond character[78]. The radical monoanionic character of dithiolene ligand has been studied extensively and both theoretical and practical evidence for this form has firmly been established [77-78].

When π orbitals of reacting dithiolene ligands interact with dπ orbitals of a transition metal ion in order to form a metal dithiolene complex, then mixed ligand and/or metal character-like frontier molecular orbitals are generated and a certain extent of aromatic character is developed in that metal dithiolene complex. In general, both the metal dithiolene complexes and free dithiolene ligands often exhibit various oxidation states. According to bonding descriptions, the metal bis(dithiolene) complexes can exist as the following resonance hybrid forms with different oxidation states of central metal ion (Fig. 5)[30,55]. In general aspects we can classify the dithiolene complexes into two categories as follows:

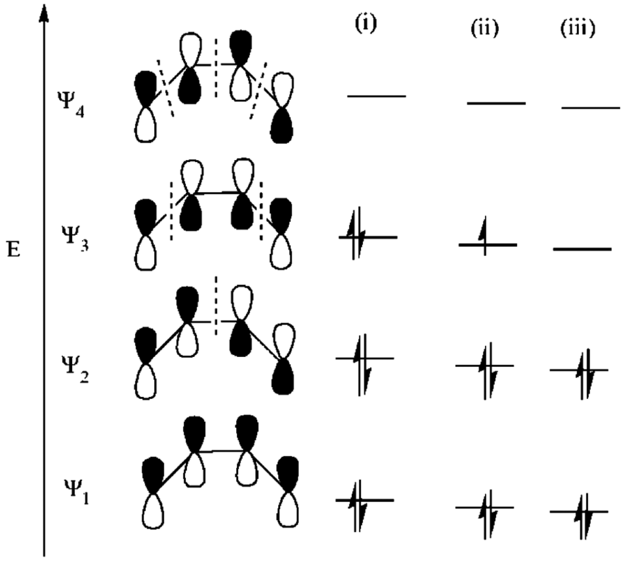


Fig. 4 — Schematic representation of FMO bonding approach and electron occupancy in (i) ene-1,2-dithiolate; (ii) radical monoanionic form and (iii) 1,2-dithione

Homoleptic dithiolene complexes

Homoleptic dithiolene complexes can be further classified into two categories as follows (Fig. 6)

Metal bis(dithiolene) complex: This type of complex is formed either with square planar geometry (with metal ion having electronic configurations of d^4, d^8, d^9) or distorted tetrahedral geometries (with metal ion of electronic configuration of d^{10}) [25(a)].

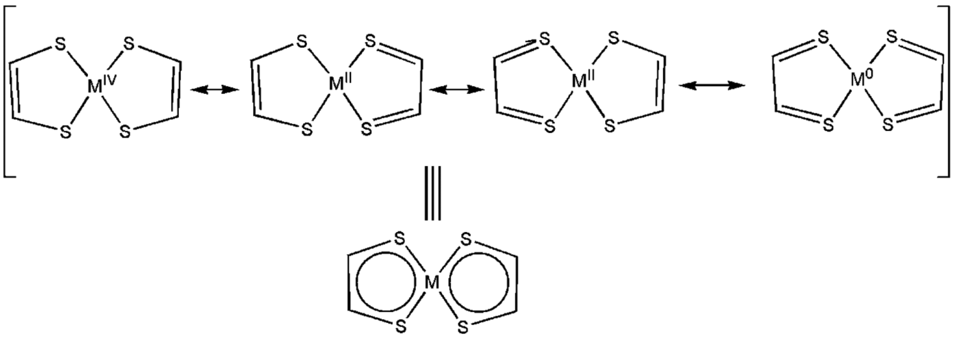
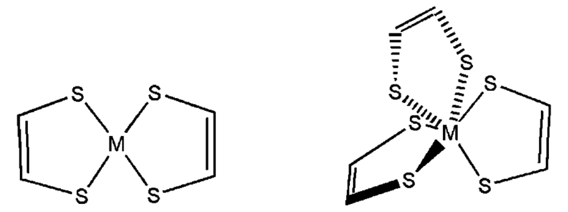
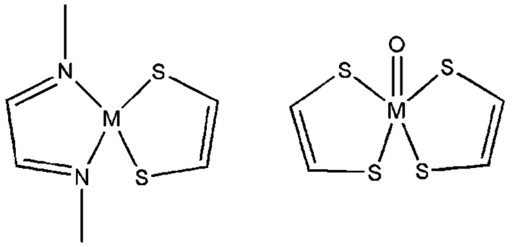


Fig. 5 — Different resonance hybrid forms of metal dithiolene complex with variable oxidation states of central metal ion[30, 55]



Metal bis(dithiolene) complex Tris(dithiolene) complex

Fig. 6 — Homoleptic metal dithiolene complex[25]



Metal(dithiolene)(diimine) Metal-oxo(dithiolene)$_2$

Fig. 7 — Heteroleptic metal dithiolene complex[26, 27,28, 29]

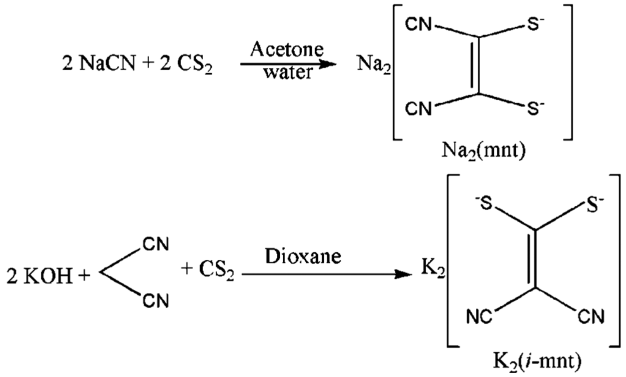
Metal tris(dithiolene) complex: This type of complexes are usually observed, with octahedral geometry (with metal ions of Group-4,7-9) and trigonal prismatic geometry (with metal ions of Group-5-7) [25(b)].

Heteroleptic dithiolene complexes

In this type of complexes, metal ion (generally Group 6 and Group 10 metal ions of the Periodic Table) simultaneously coordinates with a dithiolene unit and an another ligand part (Fig. 7) [26-29].

Synthesis of metal bis(dithiolene) complexes

For the synthesis of transition metal bis(dithiolene) complexes several synthetic protocols are followed over the years. Out of several procedures four major synthetic pathways are discussed below. Apart from those there are many unparallel and complicated methods available for the synthesis of dithiolene complexes. Those are appended below.



Scheme 1 — Synthesis of *mnt* dithiolene ligand system and its isomer[31]

Reaction with ethylene dithiolates

To obtain ethylene dithiolates, now a days, various synthetic procedures are available. Besides, many aromatic as well as aliphatic dithiols are stable and commercially available for this purpose, but most of the other dithiols of this category are very much prone to polymerize itself rapidly and also decomposes[30].

To overcome this problem, first of all the dithioles are converted to different Na or K salts of the ligand like *cis*-1,2-dicyano-1,2-ethylenedithiolate (*mnt*) (Scheme 1) [31]. This was first developed by Bahr and Schleitzer in 1957, and the isomer 1,1-dicyano-2,2-ethylenedithiolate (*i-mnt*) was prepared for the first time in 1968 by Jensen and Henriksen[31].

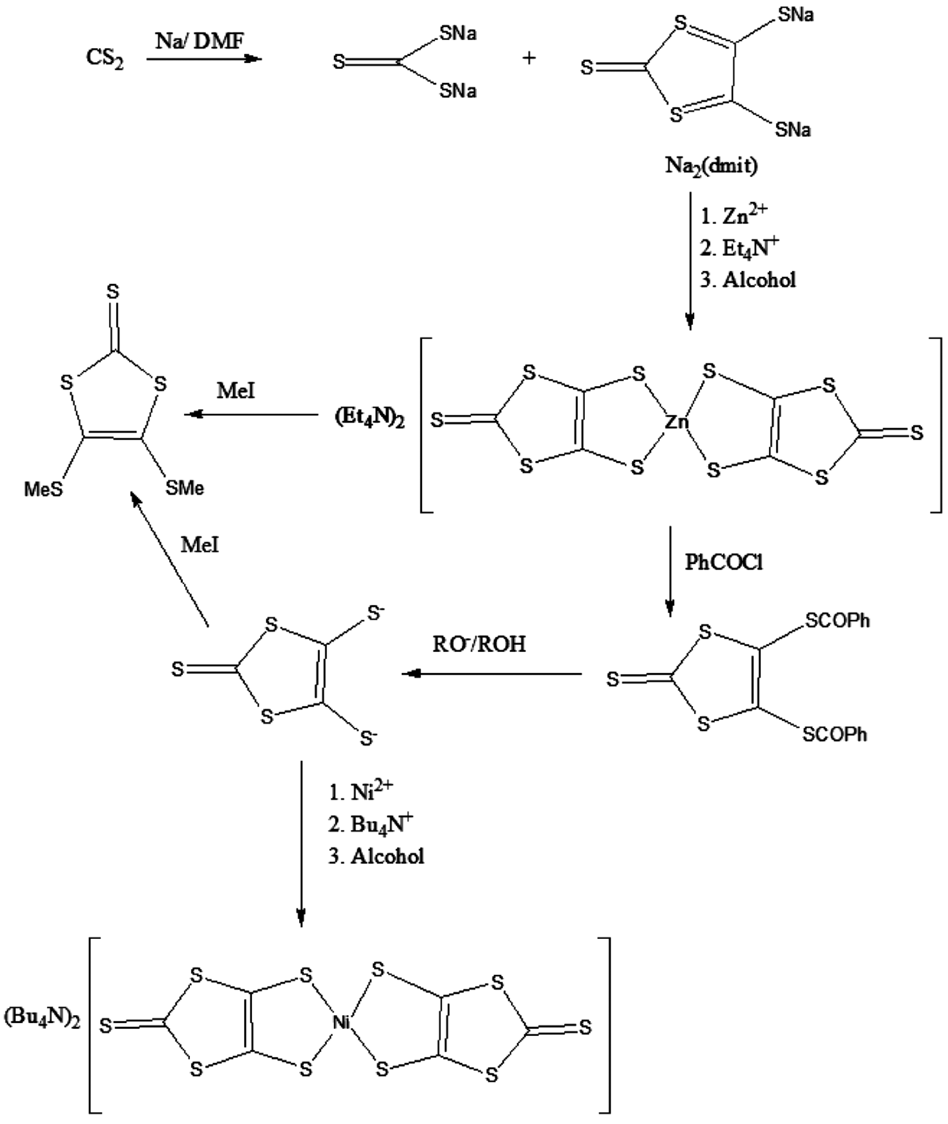
The dithiols can also be prepared from the ligands like 1,3-dithiol-2-thione-4,5-dithiolate (dmit^{2-}) and the unstable dmit^{2-} can be isolated as salts of large organic cations like Bu_4N^+ or Tetraethyl ammonium cation (Et_4N^+) [32,33]. The chemical preparation of dmit^{2-} ligand associates the treatment of carbon disulfide (CS_2) with metallic sodium in dimethylformamide (DMF) solution resulting the mixture of trithiocarbonate (CS_3^{2-}) along with $dmit^{2-}$. The resulting $dmit^{2-}$ can be isolated as the ammonium salt of $[M(dmit)_2]^{2-}$ (Scheme 2).'dmit' ligand based other metal dithiolene complexes can also be prepared from $[Zn(dmit)_2]^{2-}$ by the exchange of ligand or by the metastasis reaction with Na_2dmit. In comparison to alkali salts of $dmit^{2-}$ the salts of $[Zn(dmit)_2]^{2-}$ are much more air stable [32].

Reaction with α-haloketones

Reaction of α-haloketone with metal complexes like L*n*M$(SH)_2$(L*n*= Bis(diphenylphosphino)ethane (dppe); M= Ni, Pd, Pt) yields the corresponding dithiolene complex (Scheme 3). This method was particularly helpful for the synthesis of dithiolene complex of substituted pyridine based ligands[34-36].

Reaction with dithiones

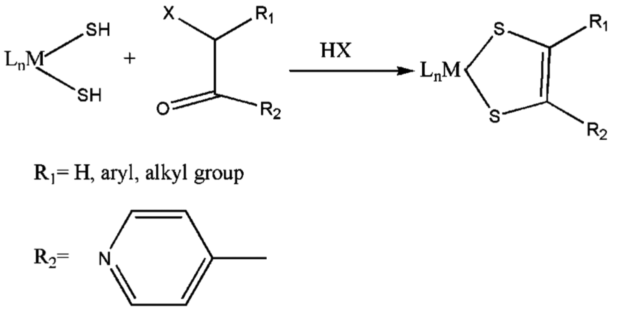
This is an old but still one of the most powerful methods for producing large scale homoleptic dithiolene complexes like $Ni(S_2C_2R_2)_2$ [where R= Me, Ph]. 1,2-dithiones can be obtained *in situ* directly by the reaction of 1,2-diones or acyloins with P_4S_{10} in an inert solvent like 1,4-dioxane followed by hydrolysis with metal salt. After the completion of the reaction, the resulting mixture was generally cooled for several hours to obtain the crude material. Purification was carried out further to obtain single crystal of the metal bis(dithiolene) complex (Scheme 4)[37,38] . The reaction proceeds through *in situ* preparation of thiophosphoric ester. Recently the mechanism of the formation of thiophosphoric ester of 1,2-dithione was explained by Arumugam[40].



Scheme 2 — Synthesis of *dmit* dithiolene ligand and its metal complex[32]

Reaction with benzene poly thiols

Mainly liquid-liquid interfacial synthesis technique is applied for this type of metal dithiolene complex synthesis. An improved and interesting methodology deals with reaction with haloarenes. Firstly the halogen groups of arene nucleus are substituted with the reaction of benzyl/alkyl mercaptan in DMF solution with metallic sodium followed by the dealkylation of –SR (R = Benzyl or alkyl group) group to generate free –SH group around the arene nucleus. Later suitable metal salt is added in order to develop the metal dithiolene complex (Scheme 5) [41,42,74].



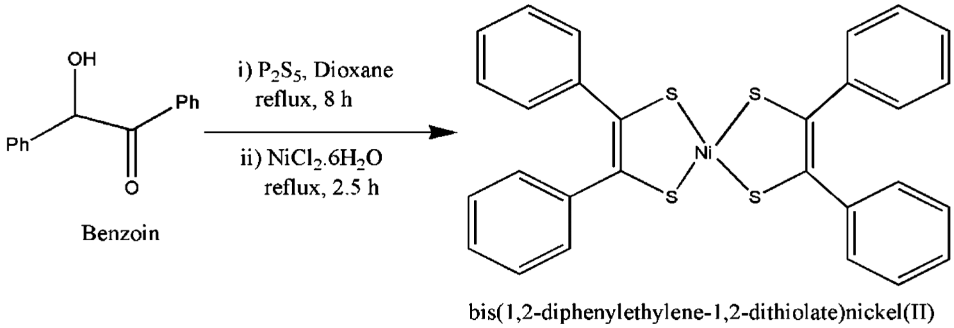
Scheme 3 — Synthesis of metal dithiolene complex from α-haloketone[34, 35, 36]

Some physicochemical properties

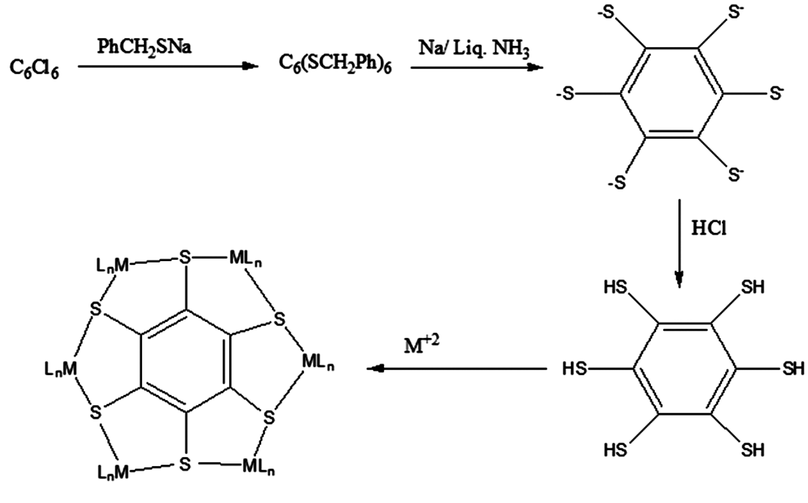
Dithiolene complexes are of special category in the field of inorganic/coordination chemistry, which has diverse field of chemical applications with its unique chemical and physicochemical properties (such as electrical conductivity, bulk ferromagnetism, NLO property and behaviour like Q-switching dyes, NIR absorbance, reversible redox activity etc.). In this review we will discuss some aspects over solid-state electrical conductivity and NIR absorbance of metal dithiolene complexes.

Electrical conductivity

To exhibit electrical conductivity for any molecular solid in solid state, electron transfer is a must and prerequisite criterion. The investigation on the electrical conductivity study of metal dithiolene complexes was found to be initiated very long time ago[43].



Scheme 4 — Synthesis of metaldithiolene complex from 1,2-dithione[37, 38]



Scheme 5 — Synthesis of benzene hexathiol (BHT) ligand based metal dithiolene complex[41, 42, 74]

Most of these synthesized dithiolene complexes, which were reported at very early days of research, generally exhibit low electrical conductivity at room temperature ranging from 10^{-3} S/cm to 10^{-15} S/cm. Since then metal dithiolene based electrically conducting molecules are being tried to be explored and developed, preferably of semiconducting in nature. Notably the molecule $(per)_2[Pt(mnt)_2]$ was the first reported complex to exhibit metal-like conductivity. This was characterized in 1980[44].

Transition metal bis(dithiolene) complexes are excellent candidates for exhibiting solid-state electrical conductivity particularly in semiconducting region [14-16,38,39,42]. Studies over the past few years has provoked it to be a good electrical conductor when coupled with ‘organic metal’ systems like tetrathiafulvalene (TTF). tetracyanoquinodimethane (TCNQ), perylene, TTF, etc (Fig. 8)[44]. Here the conductivity data of some perylene based dithiolene complex has been listed in Table 1.

The ligand 5,6-dihydro-1,4-dithiin-2,3-dithiolato ($Dddt^{2-}$) was also a good candidate for this purpose [46]. Using the isolobality concept it can be concluded that dithiolene complexes are electronically and structurally isolobal with bis(ethylenedithio) tetrathiafulvalene (BEDT-TTF) molecule (Fig. 9). This can be used for developing organic semiconductor. The conductivity data of some $dddt^{2-}$ based dithiolene molecule has been listed below in Table 2.

Among different dithiolene ligands, the $dmit^{2-}$ ligand was extensively used for developing new metal dithiolene system, which proved to be a precursor for excellent electricity conducting molecule. In recent years new aspects of molecular conductors has been developed. From the research outcome it has been observed that either changing or modifying the structure of ligand changes the conducting properties. In 1986 it was reported that the compound $(TTF)[Ni(dmit)_2]_2$ can exhibit superconductivity at 1.62 K under 7 Kbar [48]. Interestingly, in this case the tetrabutyl ammonium cation (Bu_4N^+) was replaced by TTF. Here the electrical conductivity of $dmit^{2-}$ based dithiolene complexes are listed below in Table 3. Though a large number of Pd-based dithiolene complexes of organic cation like Bu_4N^+ have been prepared, but a few of them can exhibit metal-like behaviour. Among them $(Bu_4N)_x[Pd(dmit)_2)]$ (x = 0.33 or 0.50) was reported first [50.]

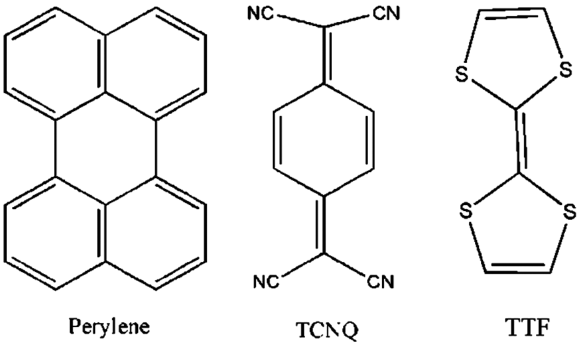


Fig. 8 — Some organic precursors for synthesis of dithiolene based organic semiconductor[44]

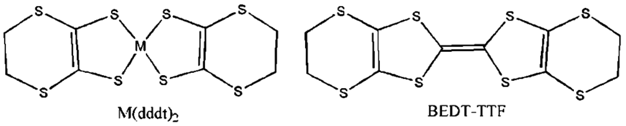


Fig. 9 — Some organic precursors for synthesis of dithiolene based organic semiconductor[46]

Table 1 — Conductivity data of some perylene based dithiolene complexes

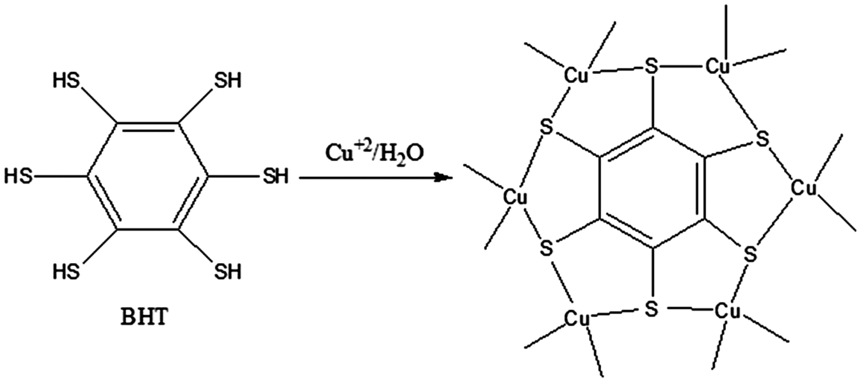
Complex	Conductivity (S/cm) at room temperature	Metal-Insulator trasition (MI)	References
$Per_2[Au(mnt)_2]$	700	MI at 12.2 K	45
$Per_2[Co(mnt)_2]$	200	MI at 73 K	45
α-$Per_2[Cu(mnt)_2]$	700	MI at 32 K	45
$Per_2[Pd(mnt)_2]$	300	MI at 28 K	45
$Per_2[Pt(mnt)_2]$	700	MI at 8.2 K	45
$Per_2[Co(mnt)_2]$. 0.5 (CH_2Cl_2)	60	MI at 272-277 K	45

Table 2 — Conductivity data of some $dddt^{2-}$ligand based dithiolene complexes

Complex	Conductivity (S/cm) at room temperature	Metal-Insulator Transition (MI)	References
$[Ni(dddt)_2]_3(HSO_4)_2$	60-300	Metallic 300-25 K	47
$[Pd(dddt)_2]_2PF_6$	1	MI at 220 K	47
$[Pd(dddt)_2]_2SbF_6$	1-2	MI at 200 K	47
$[Pd(dddt)_2]_2SnCl_x$	1	MI at 140 K	47

Table 3 — Conductivity data of some dmit^{2-} ligand based dithiolene complexes

Complex	Conductivity(S/cm) at room temperature	Metal-Insulator Transition (MI)	References
$(HMe_3N)_{0.5}[Ni(dmit)_2]$	140	MI at 220 K	49
$K_{0.4}[Ni(dmit)_2]$	10-230	MI at 20 K	49
$Cs[Pd(dmit)_2]_2$	200	MI at 70 K	49
α-$(Et_4N)_{0.5}[Au(dmit)_2]$	500	Metallic down to 1.5 K	49
β-$(Bu_4N)_x[Au(dmit)_2]$	30	Metallic down to 1.5 K	49
δ-$TTF[Pd(dmit)_2]_2$	100	MI at 120 K	49



Scheme 6 — Synthesis of $[Cu_3(BHT)]_n$ coordination polymer[42]

Recently it has been reported by the present authors' group that the metal dithiolene complexes exhibit a lower range of electrical conductivity at room temperature, whereas by increasing temperature, the electrical conductivity of this complex was increased [38,39].

Very recently BHT based dithiolene complexes[41,42] has drawn the attention for developing 2D metal dithiolene films of very high conductivity. Previously, this type of work was reported by Yip *et al.*[53]. In 2015 it has been reported that Cu-benzenehexathiol (BHT) films $[Cu_3(BHT)]_n$ exhibit a room temperature conductivity of 1580 S/cm (Scheme 6) [42], which is the highest value of electrical conductivity, ever reported for this type of metal dithiolene based conducting polymer. The polymeric film has been developed at the liquid-liquid interface of two immisible liquids and also behaves like a ambipolar transporter with such extremely high solid-state electrical conductance.

From structure elucidation study of Cu-BHT polymeric films, it was clear that the lattice structure was actually of six fold symmetry, where the central metal atom is Cu(II), through which one BHT unit was connected with another six BHT units. Very recently Cu-BHT polymeric films, with high electrical conductivity (10^3 S/cm), was also used as hydrogen evolution catalyst [57].Quite interestingly, despite the use of BHT as a golden template, only one dithiolene ligand i.e. dmit^{2-}beautifies the search for dithiolene based semiconductor much more better over the years, and also lead researchers to develop dithiolene ligand based superconductors [51,52].

In most of the cases of dithiolene complexes, the involvement of sulfur enriched dithiolene ligands through the intermolecular S…S interactions, stronger overlap of sulfur d orbitals, extended aromaticity in lattice structure due to strong π-d interaction are thought to be responsible for such conducting behaviour. In recent days, studies on different dithiolene based metal complexes with high electrical conductivity [58-64] magnify this voyage. This type of metal dithiolene complexes can be very useful as an excellent candidate for developing different electronic and optoelectronic devices. Different transition metal based dithiolene complexes with such high electrical conductivity can be synthesized by changing the ligand structure with suitable substituents and altering the band gap, side by side designing of high organic insulator, 2D coordination polymeric film with semiconducting property and high carrier mobility are of recent interest and nicely accounted by Kusamoto *et al.* [79].

Near infrared (NIR) absorption

In the optical spectrum band the NIR range covers from 800 nm to 1200 nm. In recent time, metal bis(dithiolene) complexes are of maximum interest due to its unique and recent application as NIR absorbing dyes and NLO properties. In this review our interest of focus will concentrate on the discussion with designing of suitable metal bis(dithiolene) complexes and its present application. The unique structural and chemical features of metal bis(dithiolene) complexes helps them to present as an excellent candidate for the study of NIR absorption [65-73].

For NIR absorption study, the dithiolenes are of recent interest for researchers, due to its broad and intense characteristics of electronic transition of longer wavelength (above 800 nm), which is quite difficult to observe in other transition metal based compounds. In most of the cases of transition metal based compounds low energy electronic transition arises for weak d-d transition(s). For metal dithiolene complexes, the relatively longer wavelength electronic transition arises due to Ligand to Metal Charge Transfer (LMCT) transition $[L(\pi)\rightarrow d(\pi^*)$ transition] and this type of transition favours more if the energy gap between Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) decreases. The strong NIR shift of metal dithiolene complexes is well dependent on the extensive π-electrons delocalization of dithiolene backbone as well as the availability of d-orbital of central metal ion. Promotion of an electron (by absorbing sufficient photon energy) from bonding M.O. (HOMO) to antibonding M.O. (LUMO) can be explained on the basis of Linear Combination of Atomic Orbitals-Molecular Orbitals theory. Due to exhibition of such very strong NIR absorption, the dithiolene systems can be used as a suitable material for producing Q-switch laser dyes [30] (which allows the laser devices to produce very intense and short pulses) for producing guest-host liquid crystals devices based upon NIR dyes [82]. The dithiolene complexes are valuable for such purpose due to their following distinct features.

a) Exhibiting delocalized electronic structure by maintaining coplanarity of ligand-π system with the metal centre (which helps for intense π-π^* transition >800 nm)

b) Variable oxidation state and redoxactivity

c) High thermal and photochemical stability

It can be stated that the following factors must be considered for a metal dithiolene complex to shift the π-π^* electronic transition absorption maxima to a relatively lower energy region (i.e. to be red shifted).

(i) Maintaining co-planarity of ligand π system with the metal centre in presence of an extended π electronic system (for sustaining extended conjugation throughout the lattice system)

(ii) Insertion of sterically bulkier group to increase solubility in particular solvent.

(iii) Alterations of the central metal ion for suitable tuning the energy gap.

Actually most of the Ni(II) based dithiolene complexes exhibit NIR absorption because of their higher delocalization possibility within these complexes compared to their Pd and Pt analogues [78.] Generally Pt(II) and Pd(II) metal dithiolene complexes exhibit some extent of hypsochromic shift and bathochromic shift, respectively compared to than that of Ni^{2+} dithiolene complexes with same ligand [82]. In this regard we must have to consider two other important factors as follows.

Designing a suitable metal bis(dithiolene) complex with particular substituents plays an important role in this field. Density Functional Theory study confirms the dependence of HOMO-LUMO energy gap with the nature of substituents with electron donating/electron withdrawing groups (Fig. 10). Substituent with electron donating group (such as methyl, ethyl, methoxy etc.) or having delocalized π- electron clouds (such as phenyl, naphthyl etc.) helps to decrease the HOMO-LUMO energy gap and facilitates the π-π^* transition, whereas substituent with electron withdrawing group generally disfavours this type of transition in NIR region. An substituent with electron donating nature shifts the electronic transition to a longer wavelength i.e. bathochromic shift absorption, in reverse, an substituent with electron withdrawing nature makes it hypsochromic shift absorption i.e. a lower wavelength (Fig. 11) [76].

(B) Nature of solvent

Nature of solvent plays an important role in the measurement of π-π^*electronic transition of metal dithiolene complex, metal dithiolene complexes are sensitive to the nature of solvent used, actually nature of coordination ability of solvent molecule affects the experimental results [75] as follows:

i) Non coordinating aprotic solvents like CH_2Cl_2, $CHCl_3$ favors the electronic transition as expected.

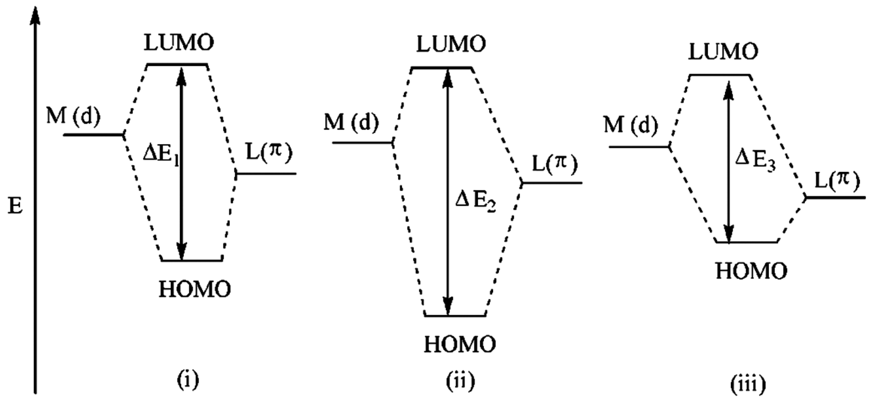


Fig. 10 — A generalized schematic representation of HOMO-LUMO energy gap (ΔE) for metal dithiolene complex. (i) with no substituent (ΔE_1), (ii) for substituent with electron withdrawing group(s) (ΔE_2) and (iii) for substituent with electron donating group(s) (ΔE_3) in dithiolene ligand backbone unit

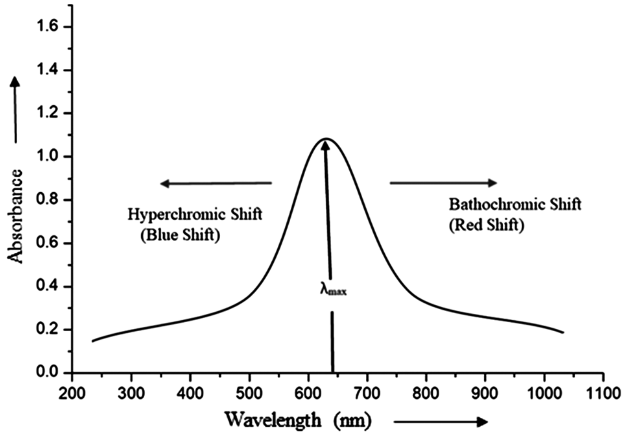


Fig. 11 — Schematic representation of blue shift and red shift in absorbance versus wavelength (nm) diagram

ii) In strong coordinating solvent like pyridine (and pyridine analogous) the NIR absorption shift disappears.

iii) In high permittivity solvent like DMF, the NIR absorption shift decreases over time.

With these ideas several symmetrical and unsymmetrical dithiolene ligands had been synthesized and extensively discussed (Fig. 12) [2,80,81]

In later stage the whole scenario (synthesis of different metal dithiolene complexes and its NIR absorbance study) was very nicely decorated by Muller-Westerhoff (Fig. 13)[30]. Earlier some Ni(II) based dithiolene complexes were reported by Zuo and his group [53,54]. Later structure dependent electronic transition of some nickel bis(dithiolene) had been greatly explored and again discussed by Zuo and his group (Fig. 14) [76]

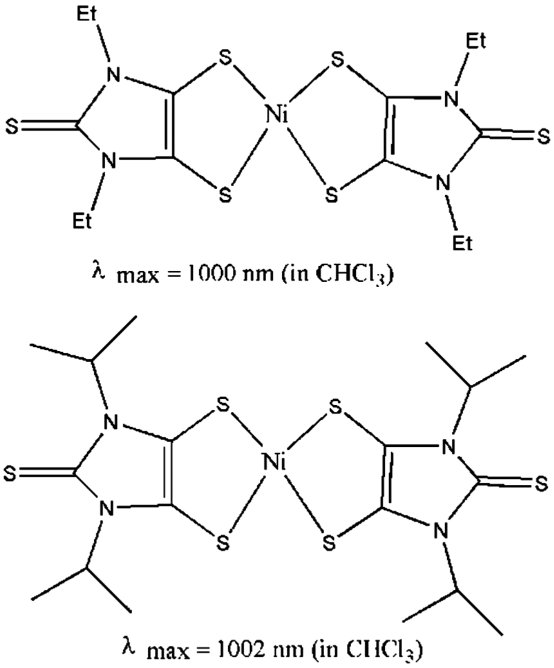


Fig. 12 — Examples of a few metal bis(dithiolene) complexes exhibiting good NIR absorption[2, 80,81]

As is evident from the investigations, it can be clearly seen that changing or even little modification on the ligand structure has a great impact on their optical properties. Insertion of a chemical moiety enriched in electron density increases the range of π-π^* transition. Redox active transition metal dithiolene complex which show strong changes in the NIR region are attracting increased research interest as NIR dyes for electro-opting switching based optical telecommunication networks. Currently this metal dithiolene complexes have also been used in biomedical science. It is reported that nickel bis(dithiolene) containing liposomes can be triggered as NIR drug delivery[56].

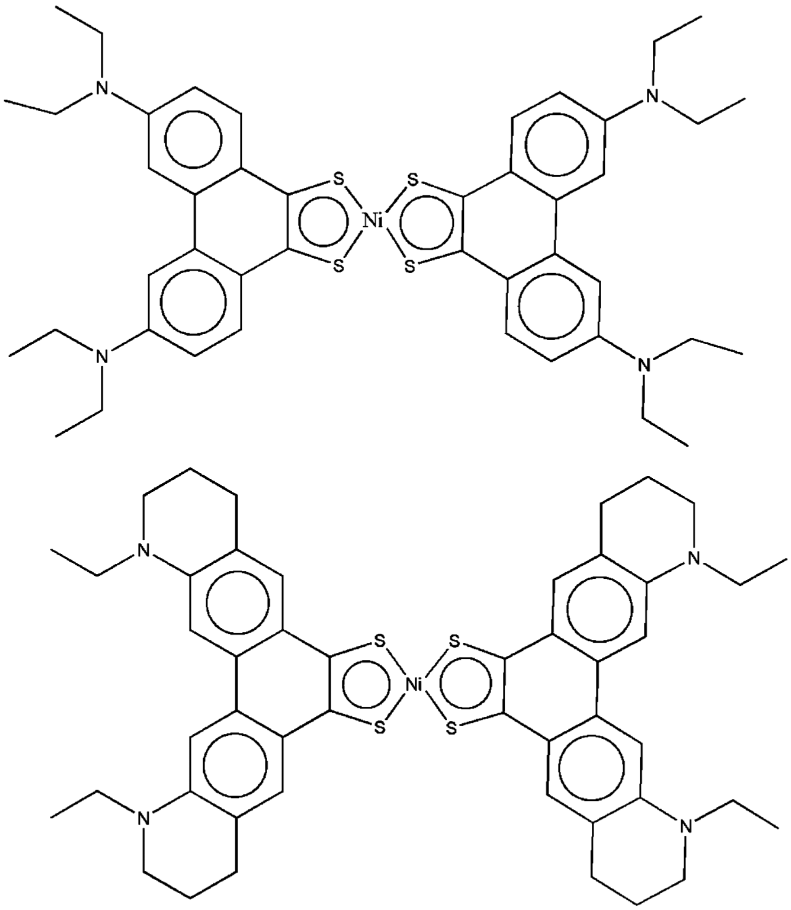


Fig. 13 — Examples of NIR absorbing metal bis(dithiolene) complexes[30] (reported by Muller-Westerhoff)

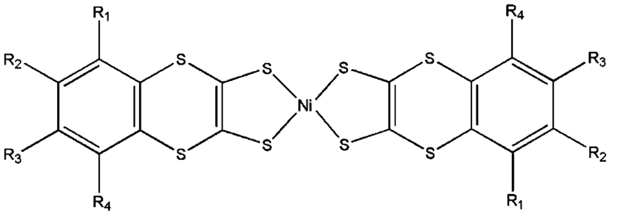


Fig. 14 — The NIR absorbing metal bis(dithiolene) complex reported by Zuo *et al.*[76]

Conclusion

In this present review, we focus on the comprehensive picture of the elementary synthesis, solid-state properties like electrical conductivity and NIR absorption studies of the transition metal dithiolene complexes. The unique physico-chemical properties of metal dithiolene complexes can be summarized as follows:

1. Dithiolene ligands are redox active. Both the dithiolene ligand itself as well as the central metal ion can possess variable oxidation state.

2. Due to presence of π-electron clouds, metal dithiolene complexes exhibit various physical properties such as electrical conductivity, strong near IR absorption bands.

Based upon the existing literature it can be summarized that a lot of work has been conducted, yet to achieve a lot more, specially based upon NIR absorption and solid-state electrical conductivity which often lead to promising photovoltaic devices, designing and developing suitable NIR absorbing probe and dye for LASER applications, developing guest-host liquid crystal devices for military applications. It is worth mentioning that in order to construct new photovoltaic solar cell, efficient NIR absorbing dyes are required. Furthermore it is expected that NIR dyes can be useful in bio-medical research, specially for bio-imaging of deep tissues (by using the π-π^* transition of the complex in NIR region). For achieving all these above condition an intense π-π^* electronic transition (by continuous modification of dithiolene unit, favourable tuning of band gaps, etc) must be the essential focus of interest. Therefore, dithiolene complexes are literally ideal material in the revolutionary fields of Science and

Technology. Moreover, further investigations are still required to design a new potentially active dithiolene based materials which can act as a promising superconductor at quite higher temperature.

In a nutshell, further studies on these metal dithiolene complexes can unravel not only its several tricky synthetic protocols and interesting properties but also can open up a new window in the chemistry of electronic and optoelectronic materials which could further trigger to move a step forward to a upcoming photo-electronic revolution.

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