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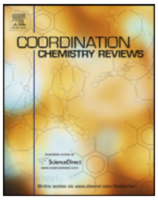

Review

Neutral d^8 metal bis-dithiolene complexes: Synthesis, electronic properties and applications

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ABSTRACT

Transition metal bis-dithiolene complexes show a large variety of physical properties such as conductivity, magnetism, optics, which render them attractive for new generations of devices. This review scans neutral d^8 metal bis-dithiolene complexes as a function of their chemical structure, and the properties that make them top-quality products for applications in the opto-electronic domain.

Abbreviations: NIR, near-infrared; UV, ultra-violet; VIS, visible; NLO, nonlinear optics; OFET, organic field-effect transistor; OL, optical limiting; ECE, electrochemical chemical electrochemical; SCE, saturated calomel electrode; 2PA, two-photon absorption; FOSC, fractional oxidation state; D–A, donor–acceptor; DFWM, degenerate four-wave mixing; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; dpedt, diphenyl-ethylenedithiolate; dpesdt, dipyridylethylsulfanyldithiolate; dmit, dithiol-thione-dithiolate or dimercaptoisotrithione; dmio, dithiol-one-dithiolate; TTF, tetrathiafulvalene; bddt, benzodithiindithiolate; dddt, dihydrodithiindithiolate; pdt, propylenedithiolate; hfdt, bis(trifluoromethyl)tetrathiafulvalenedithiolate; cddt, cyclopentanedithiindithiloate; tmdt, trimethylenetetrathiafulvalenedithiolate; dmdt, dimethylenetetrathiafulvalenedithiolate; timdt, formally the monoanion of imidazolidine-2,4,5-trithione; thiazdt, formally the monoanion of thiazoline-2,4,5-trithione; dmet, *N*-substituted 2-thioxothiazoline-4,5-dithiolato; tfdt, trifluoromethylethylene-dithiolate; dddt, dihydro-dithiin-dithiolate; pipdt, N,N′-dialkyl-piperazine-2,3-dithione; DFT, density functional theory; TD-DFT, time dependent DFT; CASSCF, complete active-space self-consistent field; DDCI, difference dedicated configuration interaction; MP2, Møller–Plesset perturbation theory (second order); MR-PT2, multireference perturbation theory (second order); MR-PT4, improved multireference perturbation theory.

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1. Introduction

Before the 1960s, metal bis-dithiolene complexes were mainly encountered in analysis of metal ions. Bis-dithiolene complexes of d^8 transition metals exhibit square-planar structures and various forms (from dianionic to cationic). Due to their remarkable coordination chemistry, until the end of the 1970s, interest lay mainly in structure, bonding and reactivity. Later on, new interests in these complexes appeared in the field of biology and more importantly in material science. The optical, magnetic, conductive, and superconductive properties displayed in these complexes have placed them among the most important families of precursors to new generations of opto-electronical devices. There are various synthetic pathways leading to metal bis-dithiolenes showing many structures aimed at numerous applications [1–14]. This review will focus on the neutral members of the series which show a very intense absorption in the visible or near-infrared region. This characteristic is a key property of these complexes. We have classified them in two main groups (homoleptic and heteroleptic complexes) defined by the substituents of the metal bis-dithiolene core (Fig. 1).

Through the variation of the substituents, properties can be tuned [15,16] and applications proposed in the field of opto-electronics, NLO or photodetection materials [17]. Lastly, we will present a brief overview of contribution of modern quantum chemistry methods to achieve an accurate description of the peculiar electronic structures of the family of the neutral nickel bis-dithiolenes, where dithiolene are well known to be “non-innocent” ligands [18]. In particular, we emphasize effects of the computational procedure on the quality of the results.

2. d^8 neutral metal bis-dithiolene complexes: which chemical structure for which property?

2.1. Homoleptic complexes

2.1.1. R family

These symmetrical metal bis-dithiolenes have been prepared with numerous alkyl or aryl substituents. Examples are given in Fig. 2.

Interest to type **1** Ni complexes comes from their ability to bind to linear alkenes in a non-conventional fashion, employing the S atoms [19], and to stand a two-electron ECE mechanism without degradation [20]. This promises significant technological breakthrough for electron-rich alkene separation and purification because the nickel bis-dithiolene system is not easily poisoned by S impurities.

Since its preparation by Schrauzer and Mayweg in [21] complex **2** and substituted derivatives were studied for many purposes:

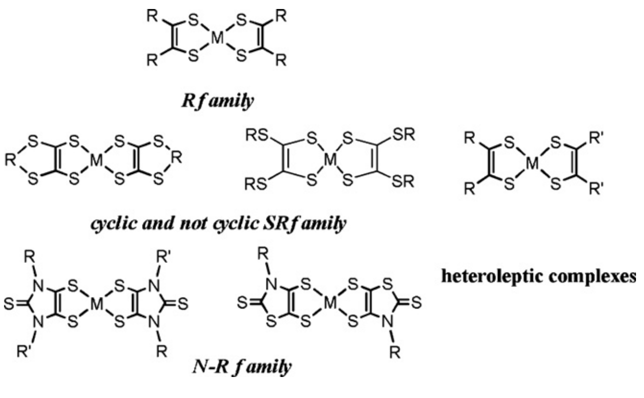


Fig. 1. Homoleptic and heteroleptic neutral bis-dithiolene complexes. The commonly used representation of the dithiolene ligand drawn here, and all over this review, is not necessarily representative of its electronic structure (*cf.* paragraph 3).

- An iterative numerical determination of the rate constants for both quenching and reaction with singlet oxygen, k_q and k_s, respectively, by dithiolato nickel complexes was developed [22]. This method was applied to the estimation of the photofading rate of cyanine dye on an epoxy resin plate.
- In the case of symmetrical or asymmetrical benzoin derivatives (α-naphthoin, furoin and α-pyridoin), the effect of the complexes on the photostabilisation of quinophthalone dye was investigated in cellulose acetate films [23].

Ni bis-dithiolene complexes with long chain alkoxy substituents ($R' = OC_nH_{2n+1}$) have mesogenic properties [15,16,24]. The absorption window offered by neutral complex **2** is also of high interest for photovoltaic applications. High electron mobilities have been recently found for these complexes [25].

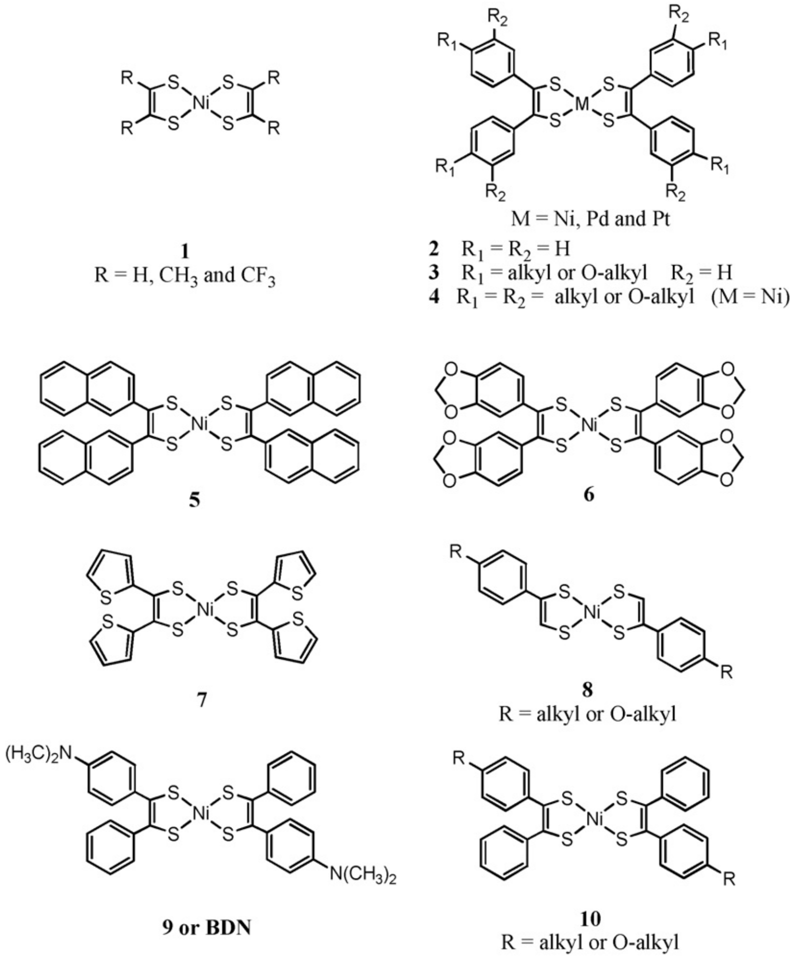
- Previous investigations of the nonlinear optical properties of these complexes have focused on third-order susceptibilities at 1.06 μm for applications in all-optical signal processing [26–29]. For a few complexes, the two-photon absorption at 1.06 μm has been measured, since nonlinear absorption is detrimental to all-optical signal processing; low 2PA coefficients were observed [30,31].

Types **3** and **4** complexes which can bear different R substituents of the phenyl rings have been widely studied by Ohta et al. [32–36]. Until then, the synthesis of the complexes, by the benzoin condensation, with alkyl/alkoxy chain-substituted benzoins proved impossible. Ohta et al. overcame this problem and succeeded in obtaining several series of alkyl- and alkoxy-substituted nickel bis(1,2-bisphenylethene-1,2-dithiolene) complexes by using the corresponding benzils as the precursors (Scheme 1).

Two series of complexes with long alkyl/alkoxy chains (C_nH_{2n+1} or OC_nH_{2n+1}) were studied [34]. They exhibit two, differently colored, discotic lamellar (DL) mesophases for $n \geq 10$. Ohta et al. [35] also studied the effect of alkoxy chain length on the discotic mesomorphism of octa-alkoxy-substituted nickel bis-dithiolene complexes. These complexes (with $n = 2–4$) had a monotropic discophase. In the case of $n = 5–12$, an enantiotropic discophase was observed. They later investigated the influence of the central metal on mesomorphism and π-acceptor properties of this family of complexes [36]. The reduction potential of these complexes does not depend on the chain length, whereas the mesomorphic properties do. Following the successful benzil method of Ohta et al., we developed new synthetic pathways to obtain asymmetric or new symmetric complexes containing linear or branched chains (Scheme 2) [37].

Types **5** and **6** complexes show strong NIR absorption and NLO properties [38]. Due to their attractive building block, the incorporation of dithiolene complexes into conjugated organic polymers offers a new possibility for the development of advanced electronic, catalytic or sensing materials. Thiophene-substituted nickel dithiolene complex **7** were anodically polymerized to give a polymer film that electrochemical properties correlated well with the neutral complex [39].

Complex **9** has been extensively studied in many domains for 30 years. Its remarkable photochemical stability under infrared radiation, associated with its high molar extinction at such wavelengths, makes this complex particularly suitable for Q switching and mode locking of high-power infrared lasers. Its first use with ruby and Nd-glass lasers was reported in 1972 [40] followed by many others works devoted to the description and improvement of the technique. In particular, **9** was the first complex to exhibit simultaneously Q-switching and degenerate four-wave mixing [41]. Its ability to carry both positive and negative charge makes it useful for organic ambipolar transistor applications [42]. Such nickel bis-dithiolene complexes-based transistors are very stable and there is no noticeable degradation even after storing in air (no encapsula-



1
R = H, CH_3 and CF_3

M = Ni, Pd and Pt
2 $R_1 = R_2 = H$
3 R_1 = alkyl or O-alkyl $R_2 = H$
4 $R_1 = R_2$ = alkyl or O-alkyl (M = Ni)

5

6

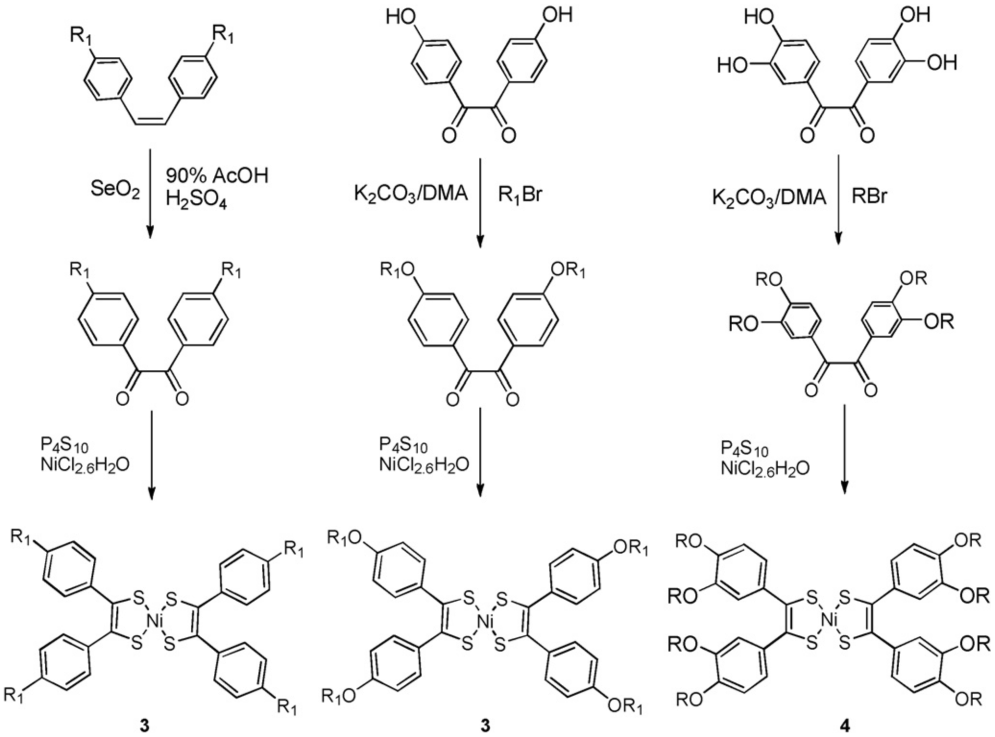
7

8
R = alkyl or O-alkyl

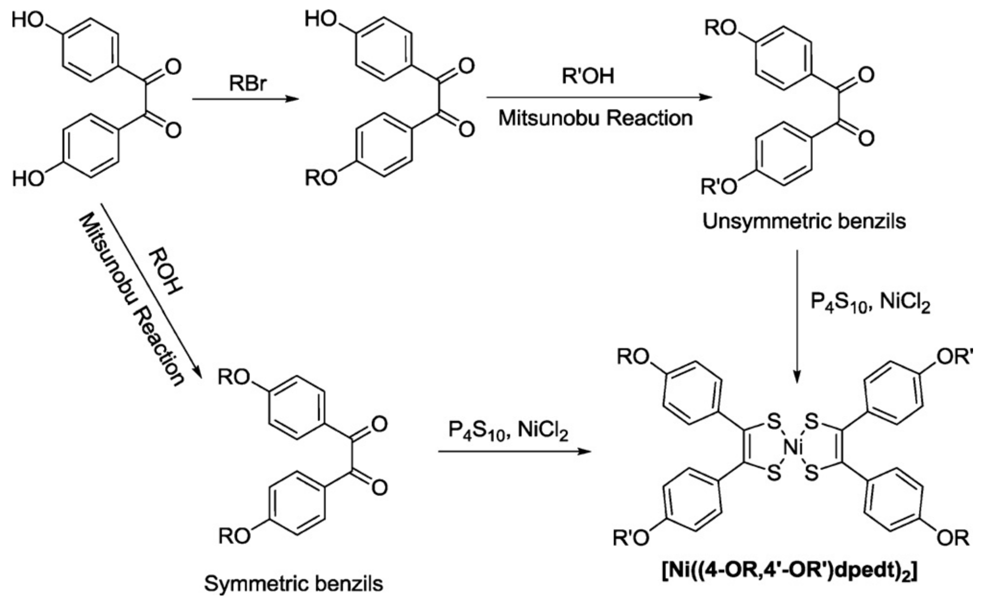
9 or BDN

10
R = alkyl or O-alkyl

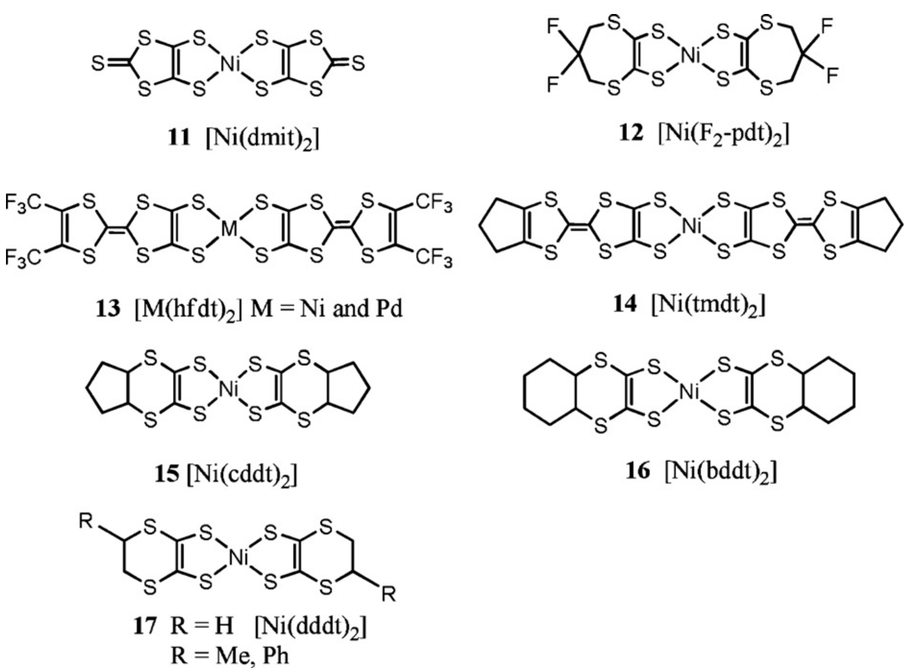
Fig. 2. Chemical structures of homoleptic $[M(C_2S_2R_2)_2]$ neutral d^8 metal bis-dithiolene complexes cited in text.



Scheme 1. Preparation of types **3** and **4** complexes.



Scheme 2. Preparation of unsymmetrical [Ni((4-OR,4′-OR′)dpedt)$_2$] complexes.



11 [Ni(dmit)$_2$]

12 [Ni(F$_2$-pdt)$_2$]

13 [M(hfdt)$_2$] M = Ni and Pd

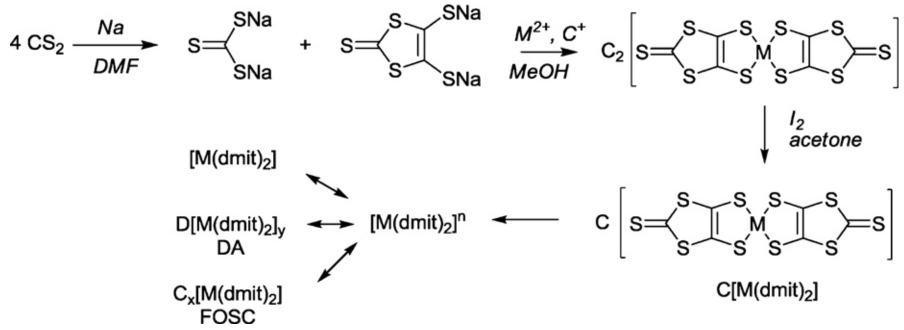
14 [Ni(tmdt)$_2$]

15 [Ni(cddt)$_2$]

16 [Ni(bddt)$_2$]

17 R = H [Ni(dddt)$_2$]
R = Me, Ph

Fig. 3. Chemical structures of homoleptic cyclic [M(C$_2$S$_2$(SR)$_2$)$_2$] neutral d^8 metal bis-dithiolene complexes cited in text.



Scheme 3. Preparation of the dmit^{2-} ligand and [M(dmit)$_2$]^n (n = zero, integer or fractional) complexes.

tion) for several months [43]. **8** and **10** have been reported in the 80s and 90s for their liquid crystalline properties [24,44–49].

2.1.2. Cyclic and non-cyclic SR family

In the complexes illustrated in Fig. 3, the bis-dithiolene core is extended by cyclic substituents. This family has given rise to famous complexes, in particular those including the dmit ligand [4,7,9], complex **12**, and extended-TTF dithiolate ligands such as in **14** and **15**.

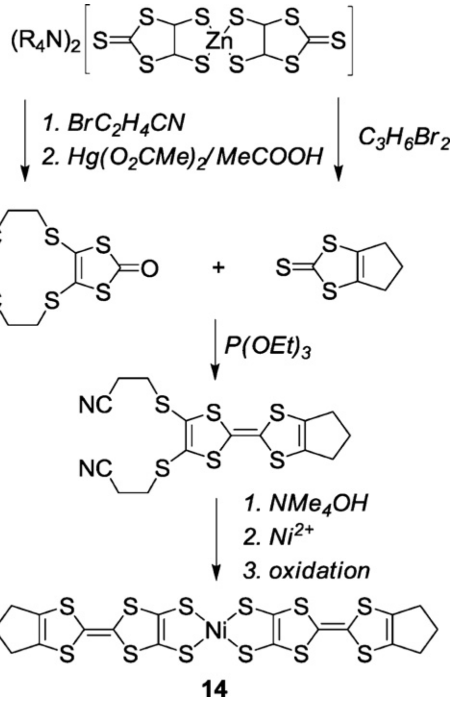
A comprehensive description of required criteria for generating molecular conductors can be found in [12,50,51]. From these works, a few comments will be given here for a better understanding of the properties of complexes **11**–**17**. In conducting materials, the flow of electrons originates from structural conditions. In conventional metals, atomic orbitals overlap enough to secure the conduction path. In materials based on molecular assemblies, the overlap of molecular orbitals is generally weak, thus not in favor of good conductive properties.

The stacking organization of planar organic molecules containing large atoms like chalcogens which enhance interactions between adjacent molecules, has proved to be efficient. However, molecular stacking is not a sufficient criterion for generating charge carriers. Stacking of planar molecules generates two bands: a HOMO-based valence band and a LUMO-based conduction band, separated by a gap which depends on the degree of interaction between the molecular orbitals. None of these bands contain free carriers. To generate conductivity, it is necessary to create partially field bands. This is typically obtained by partial oxidation/reduction of the molecules or by partial charge transfer between a donor and an acceptor molecule [9,12,51]. Based on these criteria, neutral metal complexes cannot exhibit high conductivity. Nevertheless, one family of neutral complexes containing extended-TTF dithiolate ligands shows high conductivity and metallic behaviour. In this family, partial filling of the conduction band originates from the crossing of HOMO and LUMO bands [10,12,50]. The [M(dmit)$_2$] complexes **11** are prepared as shown in Scheme 3.

They are well known as the molecules generating superconductors [12,52], and are the only metal bis-dithiolenes leading to superconductive phases: the 12 phases isolated to date [12] contains anionic dithiolene building blocks. The neutral [Ni(dmit)$_2$] complex shows a room temperature conductivity of 3.5×10^{-3} S cm^{-1} [53,54]. This neutral phase meets most of the required structural criteria for obtaining highly conducting systems, *i.e.* close regular stacking and short intermolecular contacts, but not partially filled bands, which accounts for its low conductivity at room temperature. To compare, the room temperature conductivity of the partial charge-transfer compound, TTF[Ni(dmit)$_2$]$_2$, which was the first of the 12 superconductive phases mentioned above, is 300 S cm^{-1} [55].

Attempts to increase the conductivity of neutral metal bis-dithiolene complexes used the fluorine segregation effect as a tool for controlling the solid state organization responsible for electronic properties. In the neutral gold derivative **12**, such segregation organization is observed [56], but is not efficient enough to raise the conductivity as much as in extended TTF-dithiolene complexes: the room temperature conductivity of **12** is 0.05 S cm^{-1} [50], that of [Ni(tmdt)$_2$] **14** is 400 S cm^{-1}. [10]

As a matter of fact, the best way for reaching metallic phases is to extend the π-conjugated system on ligands. Several ligands of extended-TTF dithiolate have been reported [10,57–61]. Complex **13** was the first reported extended-TTF dithiolate [57]. The nickel complex **13** is however insulating but exhibits an unusually low-energy electronic absorption at 1350 nm, considerably shifted from the characteristic absorption (800–1000 nm) found for nickel bis-dithiolene derivatives. Higher room temperature conductivities were reported for extended-TTF dithiolate complexes [58–60], more recently isolated following typically (Scheme 4). The first molecular metal, based on a single-component and neutral metal complex, [Ni(tmdt)$_2$] **14** was reported in 2001 [62]. The room temperature conductivity of **14** is 400 S cm^{-1}. Review articles report on these single-component molecular conductors [10,61,63].

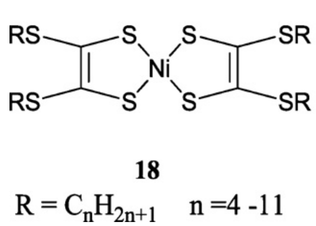


Scheme 4. Synthesis of [Ni(tmdt)$_2$] **14**.

One characteristic of the chemical structure of **11**–**16** complexes is the extension of the dithiolene core by additional saturated or unsaturated cycles. We just reported that good conducting properties are encountered for complexes showing extended π-delocalization, *i.e.* unsaturated additional cyclic substituents. They also exhibit high thermal and photochemical stabilities. Thus, third-order optical nonlinearity and optical limiting (OL) ability have been investigated in nickel complexes as **15** and **16** [64,65]. An ideal optical limiter should be transparent under laser radiation of low energies and opaque at high energies.

The complexes, most studied as optical limiters, are fullerenes (C$_{60}$) [66–68] and phthalocyanine complexes [69–71]. Ji et al. report that the optical limiting ability of **15**, measured at 532 nm with nanosecond (ns) and picosecond (ps) duration laser pulses, is better than that of C$_{60}$ in ns measurements while it is nearly the same as that of C$_{60}$ in ps measurements [64]. The limiting threshold was measured as 0.12 and 0.09 J cm^{-1} for **15**, under ns and ps laser pulses, respectively. Using the same experimental conditions, the limiting thresholds of C$_{60}$ are determined to be 0.20 and 0.10 J cm^{-1}. **15**, is more transparent than C$_{60}$ under laser radiation of low energies and more opaque at high energies. The observed optical limiting behaviour of **15**, can mostly be attributed to nonlinear absorptive processes. The limiting thresholds of **16**, were reported by Bai et al. [65] to be comparable to those observed in C$_{60}$. In addition, **16**, shows remarkable absorption in the near-IR region (ε ~63,000 dm^3 mol^{-1} cm^{-1} at 1035 nm) and is an excellent candidate as a near-IR dye for Q-switching neodymium lasers.

Nonlinear optical effects in complexes **17** have been observed and are explained by excited-state absorption and refraction. Such complexes for which the absorption is dependent upon the intensity of the input beam are promising for optical limiting applications in the visible and near-infrared spectral region [72]. Beside this, their electrical conductivities as compacted pellets are of the



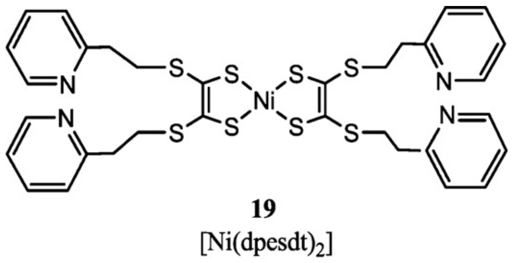
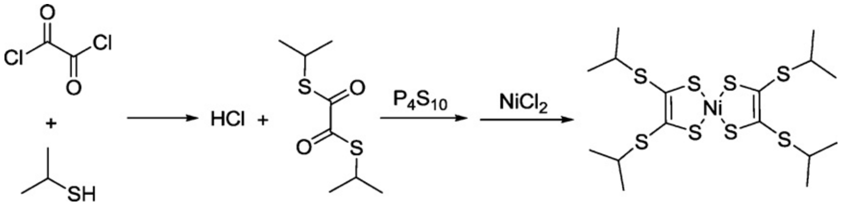


Fig. 4. Chemical structures of nickel bis-dithiolene complexes bearing linear thioalkyl substituents with long chains **18** and [Ni(dpesdt)$_2$] **19**.



Scheme 5. Preparation of complex **18** by Song et al. [78].

order of 10^2 better than their mono-anionic analogues [73], due to more favorable interactions between the neutral molecules as revealed by the crystal structures [73–75]. In the structure of neutral [Ni(phdt)$_2$] (**17**, R = Ph), the molecules are arranged as two differently oriented uniform stacks [35]. The shortest S–S contact is 3.6876 Å is about the sum of the van der Waals radii (3.70 Å) and occurs between the outermost S atoms of molecules located in adjacent stacks (inter-stack contacts). The large separation between stacks is due to the presence of phenyl on the external part of the ligand. This is consistent with the low conductivity of this complex: 1.5 10^{-6} S cm^{-1}. As no such inter-stacks interactions occur in the mono-anionic analogues, their conductivity is lower [75].

The SR family also comprises a large series of complexes in which the dithiolene core is substituted by linear SR group [76–78]. Complexes **18** are representative examples of this series, where R contains long alkylthio chains (Fig. 4).

Complex **19** is the first example of a tetra-azo substitued bis-dithiolene nickel complex. This ligand offers the possibility of coordinating both by S and N sites, which have different metal coordination abilities [79].

Experimentally, the presence of more or less long alkylthio chains in **18** increases the solubility of the complexes in various solvents, an essential property for the processability of metal dithiolenes for all optical devices use. Song et al. [78] described for the first time in three steps the continuous production (Scheme 5) of a new complex-type near-infrared chromophore applied to a near-infrared cut-off filter for plasma display television (PDP TV). The final product was efficiently produced, in a microreactor and a tubular reactor in series, using nickel chloride solution and dithiolene synthesized from thionation in a batchreactor.

Marshall et al. have published a comparative study of such a series of complexes [77] for applications in guest-host liquid crystal (LC) devices operating in the near- to mid-IR region. The lack of near-IR dyes with appropriate properties limited the development of this project. Neutral complexes **18** may overcome these difficulties: they are highly stable, possess liquid crystalline phases, can exhibit high solubility (up to 10 wt%) in LC hosts constituted of commercial products, the Merck E7 (a mixture of 4-cyano-4′-alkylbiphenyl (C5 and C7 alkyl chains), 4-cyano-4″-pentylterphenyl and 4-cyano-4′-octyloxybiphenyl) and Merck CB15 (4-cyano-4′-2-methylbutylbiphenyl). They can have melting points below room temperature allowing producing liquid crystal/dye mixtures with both high dye concentration and good resistance to phase separation. They also make them interesting candidates for material science in the domain of conductivity and photovoltaics. In metal bis-dithiolenes, the non-innocent role of the ligand in bonding and electron transfer shows that the redox processes are ligand- and not metal-based. Moreover, the extensive delocalization of the frontier molecular orbitals over the entire complex contributes to low reorganization energy during electron transfer, an attractive feature for photovoltaic applications. Solar cells involving the use of type **18** complexes as the acceptor layer in donor–acceptor (D–A) type cells can be envisioned. The charge separation and collection by external electrodes in D–A based solar cells is governed by the energy gap of each component of the system.

2.1.3. *NR families*

The most popular bis-dithiolene family bearing nitrogen containing substituents is built on the RR′-timdt ligand (which include an imidazoline ring) (Fig. 5, complexes **20**) [80–85].

The first [M(timdt)$_2$] complexes were prepared in the 90s and contained one single type of R substituent (Scheme 6) [80,81,86]. Complexes including two different R groups can be prepared following the same procedure [87].

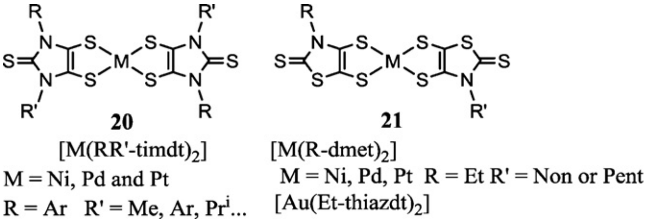
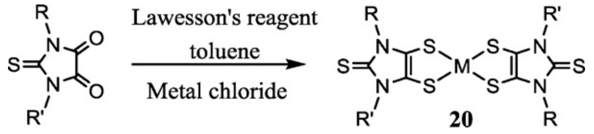


Fig. 5. Chemical structure of [M(RR′-timdt)$_2$] **20** and [M(R-dmet)$_2$] **21** also called [M(R-thiazdt)$_2$] neutral d^8 metal bis-dithiolene complexes cited in text.



Scheme 6. Preparation of [M(RR′-timdt)$_2$] 20.

This series affords materials with high thermal and photochemical stability at laser wavelength. The imidazole extension maintains the planarity of the molecule. The symmetrical d^8 neutral complexes strongly absorb in the NIR region. They are of high interest for applications in Q-switching and photodetectors [86,88].

Natali et al. have developed a photodetector by casting complex **20** onto a quartz substrate [88,89]. Due to the intense absorption of complex **20** in the NIR region (1000 nm), the device photoconductivity is enhanced when the irradiating wavelength belongs to this region of the spectrum. The device acts as an intrinsically wavelength-selective photodetector. They analysed the interrelation between the signal frequency response in this photodetector and the distribution of traps of the active materials playing a fundamental role in the transport of charge carriers.

The [M(RR′-dmet)$_2$] (M = Ni, Pd and Pt, R = Et R′ = Non or Pent) [85] or [M(R-thiazdt)$_2$] (M = Au R = R′ = Et) [90] family **21** is intermediate between (dmit) complexes **11** and (timdt) complexes **20** (Fig. 5). They show interesting properties and potentiality for optical applications due to their intense NIR absorption [85].

2.2. Heteroleptic complexes

Unsymmetrical complexes as examples shown in Fig. 6 have been developed for NLO applications; their synthesis is described in Scheme 7 [91–95].

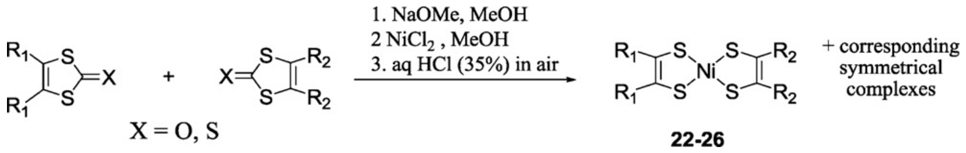
In general, C_2S_2-π-donor substituents (*push*) in symmetric complexes raise the energy of both the HOMO and the LUMO so that even the former is preferentially depopulated. This explains the stability cationic complexes where the external S atoms of the dithiolate ligand were substituted by N-donor atoms (ligand R-pipdt) [96]. In contrast, π-acceptor substituents (*pull*) lower the energy of both MOs and favor the dianionic complexes. Combination of one push and a pull ligand leads to the formation of air and light stable complexes. These asymmetrical complexes are potential second-order chromophores due to the inter-ligand charge-transfer (CT) of the HOMO–LUMO transition and most often they exhibit noticeable first molecular hyperpolarizabilities [11]. In Ref. [97], the HOMO–LUMO transition has ligand-to-ligand CT character mediated by the coordinated metal. Depending on their relative energies, a mixing between ligands and metal d-orbitals can occur, being generally significant in the HOMO and lower in the LUMO. Consequently, the HOMO–LUMO transition can be described as MMLL'CT (mixed ligand/ligand-to-ligand transition). This assignment will be discussed in paragraph 3. They recently gained interest for NLO applications. There are three main interests to study NLO complexes.

The first one is to find materials exhibiting large second harmonic generation (SHG) to be used for frequency-doubling of laser beams. Secondly, complexes showing a large value of the product βμ (where β is the first molecular hyperpolarizability, and μ is the dipole moment of the ground state) are excellent chromophores for building electro-optical (EO) polymers based devices.

The third interest is in the field of new third-order NLO materials and requires large conjugated systems to achieve this third-order effect. The nonlinear absorption β, refraction parameter γ', third-order susceptibility χ^3 of the solutions and the effective second-order hyperpolarizability γ of complexes **22**–**24** were studied. All these dithiolene complexes were found to exhibit significant nonlinear refraction, larger than the corresponding nonlinear absorption. The second-order hyperpolarizabilities γ values were found to be as large as 10^{-27} esu [93]. These complexes also exhibit strong third-order nonlinear optical response in the visible and near-infrared spectral regions [94].

2.3. Optical and electrochemical properties

The electronic properties of the complexes described in this review are summarized below in two tables which display their



Scheme 7. Preparation of unsymmetrical complexes.

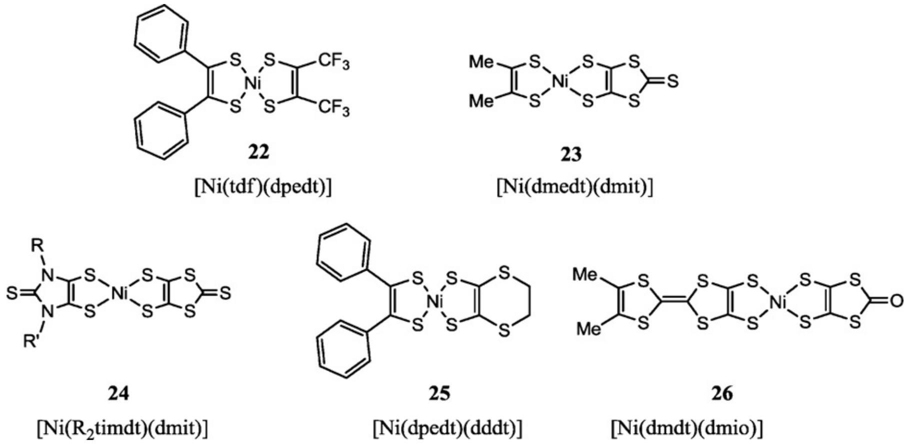


Fig. 6. Chemical structures of unsymmetrical neutral d^8 metal bis-dithiolene complexes [NiLL′] cited in text.

Table 1
Position of the maximum NIR absorption peak, corresponding extinction coefficient (ε) and solvent used for selected neutral nickel bis-dithiolene complexes.

Complex	R	λ_{max} (nm)	ε (L mol^{-1} cm^{-1})	Solvent	Ref.
1	CF_3	719	12,400	n-Hexane	[98]
2	$R_1 = R_2 = H$	866	30,900	Chloroform	[39]
3	$R_2 = H$ $R_1 = OC_9H_{19}$	925	25,100	Chloroform	[32]
4	$R_1 = R_2 = C_8H_{17}$	898	33,100	Chloroform	[99]
4	$R_1 = R_2 = OC_{10}H_{21}$	959	36,300	Chloroform	[99]
5		898	37,800	Dichloromethane	[37]
6		934	32,200	Dichloromethane	[37]
7		976	38,820	Dichloromethane	[39]
8	C_8H_{17}	830	43,000	Cyclohexane	[45]
9		1006	2.5×10^6	Dichloromethane	[40]
10	$OC_{12}H_{25}$	780	–	Chloroform	[24]
11		1001	–	Dichloromethane	[100]
15		982	46,000	Benzene	[64]
18	C_6H_5	1028	43,000	Benzene	[73]
17	CH_3	1029	36,000	Benzene	[73]
18	Ph	1006	40,130	Dichloromethane	[76]
18	C_7H_{15} and C_8H_{17}	1000	36,200	Dichloromethane	[37]
20	Et	1000	80,000	Chloroform	[81]
20	Pr^i	1002	80,000	Chloroform	[81]
21	Et	1030	–	Toluene	[101]
23		933	29,100	Carbone disulfide	[93]
24	$R = R' = Pr^i$	1056	39,000	Chloroform	[92]

absorption and electrochemical characteristics, respectively. When available, the given data have been chosen, in comparable solvents as much as possible.

Electronic absorption properties of the neutral d^8 metal bis-dithiolene complexes (Table 1): their absorption in solution ranges from 700 to 1060 nm, depending on the substituents nature. In the homoleptic series (complexes **1**–**10**), the influence of the electro donating/accepting group grafted onto the complex core is observed. The more accepting the substituent is, the lower the maximum absorption wavelength is. This is exemplified for example by considering the effect of the trifluoromethyl group (complex **1**) which leads to the lower value of λ. The same trend is observed with the substituents introduced on the phenyl ring. The λ value exhibits a red-shift (ca. 0.13 eV) when the phenylalkyl or phenylalkoxy (complex **3** or **4**) is replaced by a phenylamino (complex **9**) substituent. The number of the grafted chains has also a slight influence (see for comparison complexes **3** and **4** and complexes **3** and **10** for the case of alkoxy chains).

The SR compounds (complexes **11**–**18**), with either cyclic or not cyclic substituents, show absorption wavelengths around 1000–1030 nm. The same value is obtained with complexes containing imidazoline rings (complexes **20**), but in this case, there is a noticeable high molar absorption coefficient, twice as large as most of the others.

Electrochemical properties of the neutral d^8 metal bis-dithiolene complexes: most of these complexes show a manifest stability in their reduced or oxidized state as attested by their reversible reduction and oxidation potential values reported in Table 2.

The influence of the nature of the grafted chain is of minor effect on the potential values. This is valid for the homoleptic (compounds **2**, **3** and **4**), SR (compound **18**) or NR (compound **20**) family. The dmit ligand appears to be the easier solution to reduce complex (complex **11**) with the higher value of reduction potential. In a coherent way, complex **11** presents the higher value of oxidation potential. The dmit acts as a strong electron accepting ligand. On the other side, the timdt ligand (see complexes **18** and **20**) acts as an electron donating ligand with a relatively low oxidation potential value. The effects of both ligands in the mixed complex **24** are counter-balanced if considering its intermediate oxidation potential value. No reduction potential value is available for compound **24** preventing any corroboration of this observation. The

Table 2
Cyclic voltammetric data of selected neutral nickel bis-dithiolene complexes; half wave potentials are given in V.

Complex	R	$E_{1/2}$ (−1/−2)	$E_{1/2}$ (0/−1)	$E_{1/2}$ (1/0)	Solvent	Ref/electrode	Ref.
1	CF_3		−0.121		Acetonitrile	SCE	[98]
1	CH_3	−1.07	−0.23	1.08	1,2-Dichloroethane	Ag/AgCl	[94]
2	$R_1 = R_2 = H$	−0.86	−0.06	1.01	1,2-Dichloroethane	Ag/AgCl	[94]
3	$R_2 = H$ $R_1 = OC_9H_{19}$		−0.06		1,2-Dichloroethane	SCE	[32]
4	$R_1 = R_2 = C_6H_{13}$		−0.04		1,2-Dichloroethane	SCE	[99]
4	$R_1 = R_2 = OC_{10}H_{21}$		−0.06		1,2-Dichloroethane	SCE	[99]
7		−0.66	0.13	1.08	Acetonitrile	SCE	[39]
10			0.072		1,2-Dichloroethane	SCE	[24]
11		−0.23	0.26	1.33	1,2-Dichloroethane	Ag/AgCl	[94]
17		−0.74	−0.06	0.88	1,2-Dichloroethane	Ag/AgCl	[94]
18	C_6H_{13}		−0.08	0.76	1,2-Dichloroethane	SCE	[76]
18	C_8H_{17}	−0.78	−0.13	0.74	1,2-Dichloroethane	SCE	[37]
20	Et	−0.51	−0.06	0.83	1,2-Dichloroethane	SCE	[81]
20	Pr^i	−0.6	−0.12	0.78	1,2-Dichloroethane	SCE	[81]
21	Et	−0.38	0.15		1,2-Dichloroethane	SCE	[101]
23		−0.65	0.04	1.21	1,2-Dichloroethane	Ag/AgCl	[94]
24	$R = R' = Pr^i$	−0.4	–	1.15	Acetonitrile	Ag/AgCl	[92]
25		−0.79	−0.04	0.99	1,2-Dichloroethane	Ag/AgCl	[94]

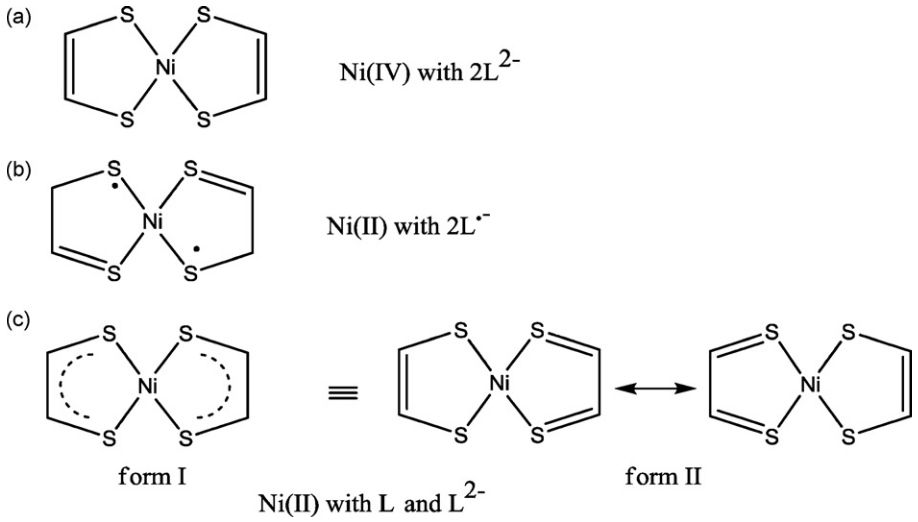


Fig. 7. The three oxidation level of dithiolene ligand (L, $L^{\bullet-}$ and L^{2-}) and metal oxidation levels for neutral nickel bis-dithiolene complexes.

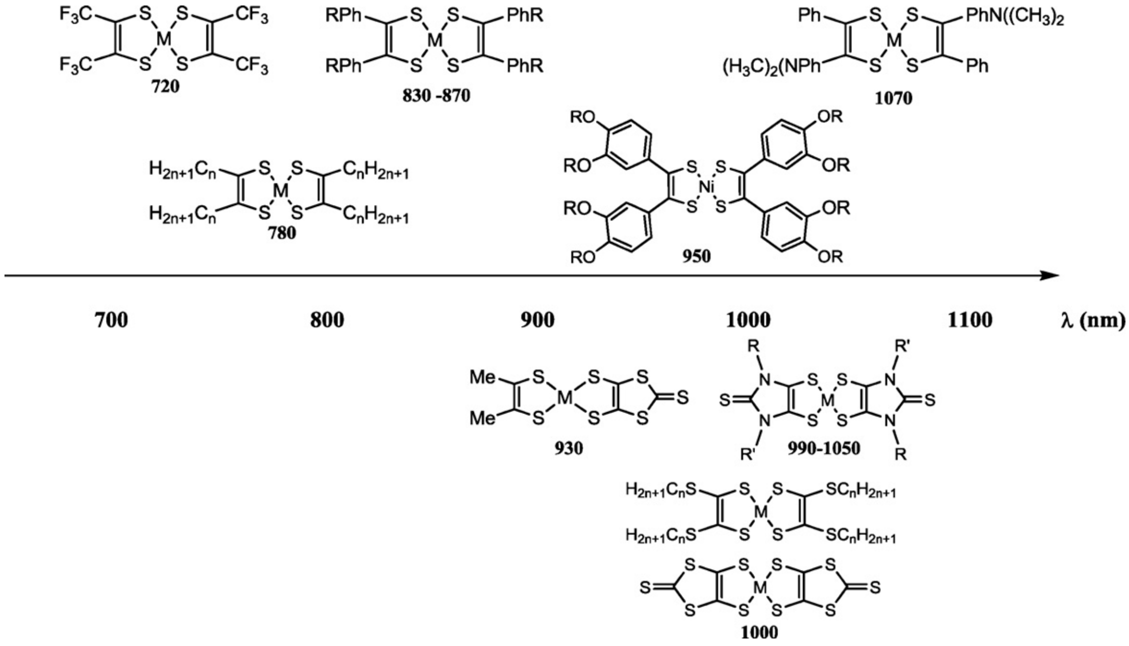
same counter-balance effect in oxidation values is exemplified by compounds **2**, **17** and **25** where compound **25** represents a mixing of compounds **2** and **17**. Surprisingly, the reduction potential value of the three compounds remains unchanged. However, this effect is clear with compounds **1** ($R=CH_3$), **11** and **23**, the latter possessing the mixed structure of the other two. Its oxidation and reduction potentials are in the intermediate of those of the corresponding compounds.

Electrochemical studies of type **18** complexes bearing linear or branched long chain alkyl groups (R = *n*-heptyl and 2-ethylhexyl), have been recently reported and show the possibility of reaching electrochemical gaps in the solid state [102]. The measured bandgaps are in the range of 0.6–0.9 eV and are sensitive to the electrochemical medium. They are smaller than the optical bandgaps which are about 1.1 eV.

3. Contribution of theoretical calculations to the comprehension of the physical properties of metal bis-dithiolene complexes

Understanding the structure of the electronics states of neutral nickel bis-dithiolene complexes has always been an important goal of theoretical research and despite very active research in this field, many questions remain unanswered. In particular, an intensely debated question is whether dithiolene ligands can exist as a neutral dithioketone (L), a radical monoanion ($L^{\bullet-}$) or a dianionic dithiolate (L^{2-}). As a consequence, the description of the nickel and ligand oxidation states is still a problem. The neutral complexes can be formulated in at least three canonical forms (Fig. 7).

After excluding the oxidation state of IV for the nickel atom [103,104] (Fig. 7a), two models for the electronic structure of these



Scheme 8. Absorption domain of various metal neutral bis-dithiolenes complexes.

complexes resulting in an oxidation state of II for the metal are discussed in the literature. Stiefel et al. proposed a diradical singlet ground state (open shell) (Fig. 7b), whereas Schrauzer and Mayweg [105] and Bach and Holm [106] proposed a singlet closed shell ground state based on either a fully delocalized structure (Fig. 7c, form I), or on two resonance hybrid structures (Fig. 7c, form II). The ability to describe the diradical character of such complexes is clearly a challenging task for quantum calculations. Theoretical work performed by Bachler et al. [107] in 2002 using broken symmetry DFT formalism [108], or more recently other works described in Refs. [104,109] exemplify the difficulties to find the most appropriate theoretical methods for the computation of properties of interest of a chosen set of nickel dithiolene molecules. Estimation of a diradical character allows discrimination between a diradical structure and a fully delocalized one for the ground state. This procedure has been applied by many groups [104,107,109,110], who discussed the diradical character of nickel complexes with different type of ligands. They have shown that broken symmetry DFT solutions and multiconfigurational (CASSCF, DDCI, MR-PT2, MR-PT4) calculations give the same trends. The stability of the diradical forms can be connected to the relative stability of the semiquinone form of the ligand [107].

Computation of absorption spectra with a detailed description of the excitations for assignment of electronic states is another important task. On the basis of extended Hückel and DFT calculations [111,112], these absorption bands were assigned as simple HOMO–LUMO single electron transitions, however more recent works emphasize that this assignment may be somewhat misleading due to the possible multideterminantal character of the ground state wave function. As a consequence, reproduction of the absorption spectra becomes non-trivial and TD-DFT methods must be used with caution. In some cases, more elaborate multireference approaches are necessary to achieve accurate results, especially in the reproduction of the very intense electronic transition displayed by neutral complexes in the vis-NIR region [109].

Concerning calculations of the structural parameters [110,114], IR and Raman Spectra [113,115], DFT methods provide high quality calculations, better than ab initio calculations at the MP2 level. The quality of the basis set and the choice of the functional have a non-negligible effect on the structural parameters and the calculated vibrational frequencies. Mean error diminishes when enlarging the basis set while much better results are obtained using hybrid functionals.

4. Conclusion

In this review, we presented a comprehensive description of the basic physicochemical properties of neutral metal bis-dithiolene complexes in solution and in the solid state and their applications. Important synthetic pathways to target these complexes have been presented. Their properties can be summarized as follows:

- They possess delocalized π-electron systems and strong near-IR absorption bands, which can be tuned by altering the metal ion and substituents.
- An important property of the bis-dithiolene complexes is their ability to exist in several clearly defined oxidation states as well as in the stable neutral form.
- This neutral form easily stands thermal or photochemical treatments, without degradation, even at their maxima absorption.

The range of potential applications based on these materials spans the whole field of thin film devices from near-infrared photodetectors, to opto-electronics or NLO, due in part to their high absorption coefficient in the visible-near-infrared region. The wide absorption window offered by these materials is exemplified through the molecules reported in Scheme 8.

Therefore, neutral metal bis-dithiolene complexes are potentially good candidates for organic electronics and opto-electronics which are evolutive fields of science and technology covering both chemistry and physics. Moreover, new electronic and opto-electronic devices using organic-based materials are attractive because such materials characteristics present light weight, potentially low cost, and easy processability. Organic photovoltaics and field-effect transistors which require charge transport as a main process may be application fields of choice for metal neutral bis-dithiolenes.

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