

## **CHAPTER 3**

### ***Strategic design of thiophene-fused nickel dithiolenes for efficient NLO response***

#### **Abstract**

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In the third chapter the NLO property of two synthesized aryl extended thiophene fused Nickel dithiolenes are studied theoretically. Based on these two systems, a systematic modification is done by substituting neutral and zwitterionic donor acceptor group at the aryl (phenyl and thenyl) ring to enlarge their NLO responses. Among the four designed systems, zwitterionic donor-acceptor group significantly reduces the HOMO-LUMO energy gap resulting an enormous hike in the first hyperpolarizability ( $\beta$ ) values. To judge their high NLO response, transition dipole moment (TDM) density is also plotted and it is found that electron dissipation occurs from one donor part to the acceptor part with a large  $\Delta r$  index value. High  $\Delta r$  index values are quantitative measurement to understand the type of transitions, and observed a charge transfer transition in case of zwitterionic systems. Hence a relationship between first hyperpolarizability and TDM is established. In order to highlight the NLO active segment in a molecule, a density analysis is also presented.

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### 3.1. Introduction

Molecular Materials with high second order ( $\beta$ ) nonlinear optical (NLO) properties have received enormous interest of the scientific community because of their multifarious applicability in optoelectronic and photonic devices<sup>98, 99</sup> as optical switching, optical communications, data storage, signal processing and optical limiting etc. One of the specific requirements related to the above applications, is to develop molecules with high NLO response. Metal dithiolene complexes are often ideal for the above-cited applications because of their unique optical and electrochemical properties.<sup>100, 101</sup> It has been found in the literature that Ni based dithiolene complexes can be potentially used as near infrared dyes for Q-switching Nd:YAG lasers<sup>102</sup> due to their high thermal as well as photochemical stability.<sup>103</sup> Dithiolenes can also be used for energy conversion<sup>104</sup> and the development of photodetectors.<sup>105</sup> Moreover they possess very long excited-state lifetimes and tunable absorption properties which make them useful for applications in photovoltaic devices.<sup>106</sup> Another important aspect about their structures is that they possess multiple stable redox states and planar geometry, an essential criteria for developing semiconductors, superconductors and molecular metals.<sup>105</sup>

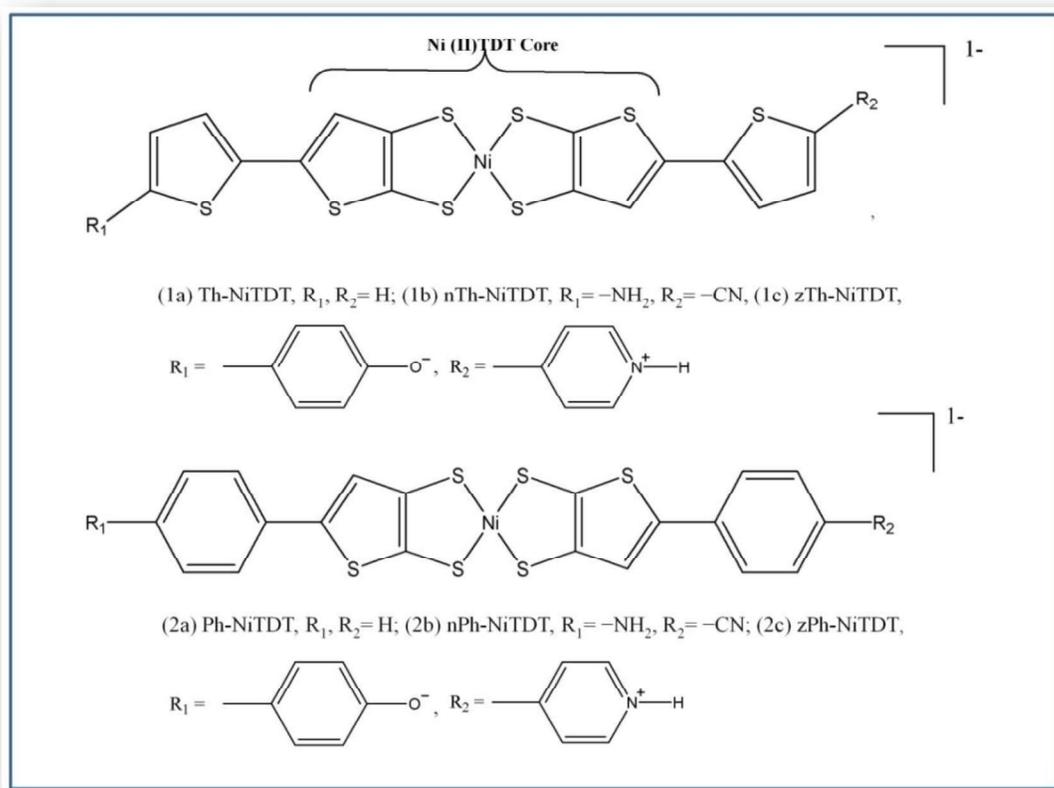
Nickel dithiolenes were first synthesized in 1960.<sup>107</sup> Since then a number of theoretical studies have been performed to understand the electronic structures and bonding schemes of these compounds. A series of interesting studies<sup>108, 109</sup> have revealed that these covalent complexes have high degree of electron delocalization. In a recent work, Herman et al.<sup>109</sup> performed INDO (intermediate neglect of differential overlap) computations for Ni(C<sub>2</sub>S<sub>2</sub>H<sub>2</sub>)<sub>2</sub> and showed that the oxidation state of the nickel atom is +2 with a d<sup>8</sup> configuration which is very common for these type of compounds.<sup>32, 110, 111</sup> Recent theoretical and experimental studies<sup>112, 113</sup> have also confirmed the previous observation in a series of Ni complexes. A more detailed presentation of properties and applications of dithiolene complexes can be found in several articles as well.<sup>103-105, 114</sup> A common tactic is to fuse aromatic rings to the dithiolene core, in order to enhance molecularity and electron delocalization.<sup>115</sup> Many fused-ring dithiolene systems have been studied so far, including fusion of benzene,<sup>116, 117</sup> functionalized benzene,<sup>118, 119</sup> thiophene,<sup>120, 121</sup> pyridine,<sup>122</sup> quinoxaline<sup>123, 124</sup> and other heterocyclic systems.<sup>125, 126</sup> Among various fused-ring dithiolene systems, thiophene-fused metal dithiolenes are of particular interest owing to their stable crystal packing arrangement. Actually, their packing arrangement is determined by the total balance of many weak intermolecular forces (hydrogen bonding, van der Waals forces,  $\pi$ - $\pi$  interactions, and S---S/M---S interactions).<sup>127, 128</sup> Additional thiophene content

would be expected to increase such intermolecular interactions and provide more significant overlap of frontier orbitals, which could result in enhanced electrical conductivity and higher magnetic transition temperatures.

In a recent report, a new family of aryl-extended nickel thiophenedithiolene complexes have been synthesized and their optical, electronic, magnetic and solid-state properties are studied as well.<sup>115</sup> It has been found that aryl-extended metal 2, 3-thiophenedithiolene can retain their planar structure even after the fusion of rings. As a consequence, the conjugation length is maximized along the molecular backbone.<sup>115</sup> These kind of Ni(II) complexes are reported to have high degree of second-order NLO response, which further increases in asymmetric compounds through push-pull mechanism.<sup>129</sup> All these facts motivate us to design nickel dithiolene based complexes for high NLO response. A well known mechanism to enhance hyperpolarizability value is to add organic donor acceptor groups to the core system.<sup>130</sup> As an example, stilbene derivatives have  $\beta$ -values of very large magnitude which is further enhanced by including the ionic donor-acceptor functional groups.<sup>131, 132</sup> Most of the studies on hyperpolarizabilities reported in the literature are on  $\pi$ -electron conjugated organic systems and there are very few reports on inorganic spacer based push-pull systems.<sup>32, 110, 111</sup> In a work by Miller et al. one zwitterionic compound in which donor (D) and acceptor (A) are linked by a sigma bond has been reported for NLO applications.<sup>133</sup> There are a number of reports in the literature<sup>134, 135</sup> in favor of the presence of crystal zwitterions structures of imidazole-1-ylacetic acid, 3-ethoxycarbonyl-2-imidazole-1-ylpropionic acid, 3-pyridinesulphonic acid which emphasizes us to choose zwitterions based substituent.

In this work, we calculate the NLO properties of Thiophene expanded Nickel thiophenedithiolene, Th-NiTDT (1a) and Phenyl expanded Nickel thiophenedithiolene, Ph-NiTDT (2a) synthesized by Amb et al.<sup>115</sup> and based on the structures (1a and 2a) a strategic design has been made (two sets) by replacing neutral and ionic donor-acceptor group as represented in Scheme 1. From the calculations it has been found that the synthesized systems (1a and 2a) possess very low values of  $\beta$  as the molecules are centrosymmetric. Keeping in mind their multifarious applicability and exceptional stability, our strategy is to modify the structure in such a manner so as to have high NLO response. We showed that by replacing the ionic donor-acceptor group at the two end of the inorganic moiety, the  $\beta$ -values enhanced by at least 10-15 times than that of the molecule without the ionic substituent. In our study, the core parts of the

synthesized systems are kept intact, rather the structures are systematically modified by annexing different functional groups to peripheral rings (Scheme 3.1).



**Scheme 3.1.** Schematic representation of the studied and designed systems.

### 3.2. Theoretical Background

The NLO properties may be defined in terms of a power of series of the molecular dipole moment in presence of an oscillating electric field according to eq 1.<sup>136</sup>

$$E = E^0 - \sum_i \mu_i F_i - \frac{1}{2} \sum_{ij} \alpha_{ij} F_i F_j - \frac{1}{3} \sum_{ijk} \beta_{ijk} F_i F_j F_k - \frac{1}{4} \sum_{ijkl} \gamma_{ijkl} F_i F_j F_k F_l - \dots \quad (3.1)$$

Here  $E$  and  $E^0$  are referred to as the energies of the perturbed and zero-field unperturbed states, the  $F_x$ 's are the field strength along a particular direction, the tensors  $\mu_i$ ,  $\alpha_{ij}$ ,  $\beta_{ijk}$  and  $\gamma_{ijkl}$  stands for the dipole moment, linear polarizability, first or static hyperpolarizability and second or cubic hyperpolarizability terms, respectively.<sup>136</sup> In general, the field as well as polarizability and hyperpolarizability terms of the above equation are frequency dependent. The first static hyperpolarizability ( $\beta_{TOTAL}$ ) may be expressed by using x, y, z components as follows,

$$\beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (3.2)$$

and

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz},$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yyz},$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}.$$

The charge density function  $\rho(r,F)$  can be explained in the powers of the field  $F$  in the same way as the expansions of energy and dipole moment.<sup>137</sup> The charge density function  $\rho(r,F)$  are expressed as

$$\rho(r, F) = \rho^{(0)}(r) + \sum_j \rho^{(1)}(r) F^j + \frac{1}{2!} \sum_{jk} \rho^{(2)}(r) F^j F^k + \frac{1}{3!} \sum_{jkl} \rho^{(3)}(r) F^j F^k F^l + \dots \quad (3.3)$$

The dipole moment expansion can be represented as follows:

$$\begin{aligned} \mu^i(F) &= -\int r^i \rho(r, F) dr^3 \\ &= \mu_0^i + \sum_j \alpha_{ij} F^j + \sum_{jk} \beta_{ijk} F^j F^k + \sum_{jkl} \gamma_{ijkl} F^j F^k F^l + \dots \\ &= -\int r^i \rho^{(0)}(r) dr^3 - \sum_j \int r^i \rho^{(1)}(r) dr^3 F^j \\ &\quad - \frac{1}{2!} \sum_{jk} \int r^i \rho^{(2)}(r) dr^3 F^j F^k - \frac{1}{3!} \sum_{jkl} \int r^i \rho^{(3)}(r) dr^3 F^j F^k F^l - \dots \end{aligned} \quad (3.4)$$

Here, the  $r^i$  is the  $i$  component of the electron coordinate. From equations (3.3) and (3.4), the first-hyperpolarizabilities can be expressed by

$$\beta_{ijk} = -\frac{1}{2!} \int r^i \rho^{(2)}(r) dr^3$$

Here,

$$\rho^{(2)}(r) = \frac{\partial^2 \rho}{\partial F^j \partial F^k} \quad (3.5)$$

This derivatives of electron densities with respect to external electric fields are referred to as  $\beta$  densities.<sup>137</sup> In this study, we confine our attention to the  $\beta$ -densities which are calculated by using the following 2<sup>nd</sup> order numerical differentiation formula.

$$\rho_{zz}^{(2)}(r) = \frac{\rho(r, F_z) + \rho(r, -F_z) - 2\rho(r, 0)}{F^2} \quad (3.6)$$

where  $\rho(r, F_z)$  represents the charge density at a special point in presence of the field  $F$ . The charge densities over a three-dimensional grid of points are evaluated by the density matrix obtained by the Gaussian 09 program package. The study of  $\beta$  densities is important as it straightforwardly highlight the NLO-active segments in a molecule.

### 3.3. Computational Details

The structures of Thiophene expanded Nickel dithiophenedithiolene, Th-NiTDT (1a) and Phenyl expanded, Ph-NiTDT (2a) complexes are taken from the crystallographic file format (CIF),<sup>115</sup> and the positions of the hydrogen atoms in the synthesized systems were partially optimized using density functional theory (DFT) based methodology with the B3LYP functional<sup>138-140</sup> in conjugation with the 6-311++g(d,p) basis set. It has been reported<sup>115</sup> that the two synthesized systems possess one unpaired electron; all the calculations have been done with unrestricted DFT formalism along with the geometry optimization for the designed systems (1b, 1c, 2b & 2c) at B3LYP functional and 6-311++g(d,p) basis set.

For calculating the  $\lambda_{\max}$  (nm) values of the synthesized systems, we have employed CAM-B3LYP/6-311g(d,p) methodology in the solution phase using the dielectric constant of the experimental solvent (acetonitrile) within polarizable continuum model (PCM) and compared our computed data with the experimentally reported excitation energies values.<sup>115</sup> Thus we have optimized the computational methodology with the help of experimental data provided for two synthesized systems (1a, 2a) and have used the same methodology for calculating excitation energies for our designed systems (1b, 1c, 2b, 2c).

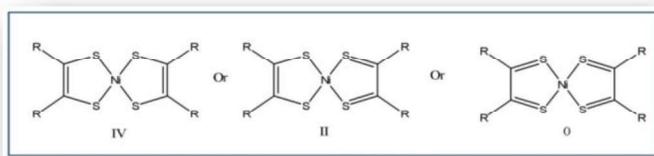
In order to highlight the NLO-active segments in a molecule, a contribution analysis<sup>137, 141</sup> has been carried out to analyze the results of the TD-DFT calculations. The NLO behavior and the first hyperpolarizability ( $\beta$ ), have been quantitatively evaluated for all the studied species by using UB3LYP/6-311++g(d,p) methodology in Gaussian 09 software.<sup>142</sup> Benchmarking of the computational model has been done with a very common push-pull system, 4-amino 4-nitro

stilbene<sup>74</sup> whose experimental first hyperpolarizability ( $\beta$ ) has been measured to be  $(260 \pm 35) \times 10^{-30}$  esu. We could, to a reasonable extent reproduce the  $\beta$  value of this system ( $184 \times 10^{-30}$  esu in gas phase) with same functional and with 6-311++g(d,p) basis set in Gaussian 09 suit of program. The correlation of our computed results with the experimentally reported data provoked us to choose this basis set and functional combination for the estimation of  $\beta$  values of our designed systems. The transition dipole moment (TDM) has been calculated based on dipole moment integral between occupied and virtual MOs. The contribution from each MO pair to the transition dipole moment can be straightforwardly evaluated and visualized with the help of Multiwfn wave function analyzer.<sup>143</sup>  $\Delta r$  index which proposed to measure the charge transfer length during electron excitation has also been calculated in Multiwfn.

### 3.4. Results and Discussions

#### 3.4.1. The electronic structure of Nickel dithiolene (NiDT)

Bisdithioglyoxalnickel,  $\text{Ni}(\text{S}_2\text{C}_2\text{H}_2)_2$ , or simply Nickel dithiolene (NiDT) is a characteristic example of square planar derivatives involving “non-innocent” conjugated sulfur-based ligands. Several bonding structures describing 8, 10 or  $12\pi$ -electron systems have been proposed for NiDT,<sup>144, 145</sup> where the formal oxidation states of Ni is 0, +2 and +4 respectively. For Ni(0) systems, the ligands are expected to retain their diketonic structure, though we hardly found any concrete evidence for such complex.<sup>146</sup> The ligands are assumed to be dithiolatodianions,  $^-\text{S}-\text{CH}=\text{CH}-\text{S}^-$  in Ni (IV) which usually occurs in  $d^8$  neutral NiDT.<sup>146</sup> NiDT is one of the first examples of complex of this family for which an assignment of the nickel

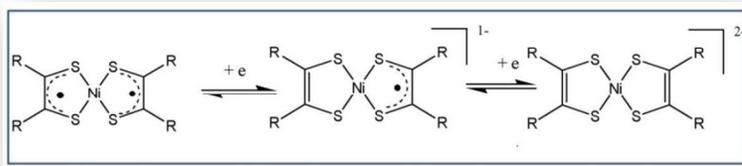


oxidation state proved to be problematic as summarized in Figure 3.1.

**Figure 3.1.** Schematic presentation of different oxidation state of NiDT complex.

A series of interesting studies regarding the electronic structure of such complex have revealed that these complexes are in fact Ni(II) complexes with each ligand bearing a radical.<sup>147, 148</sup> Calculations also showed that the frontier orbitals of such complexes are ligand-based rather than metal-based.<sup>149</sup> Because of this peculiarity, change in oxidation state in such complexes occurs at the ligand center rather than at the metal centre. This property is illustrated by the fact

that nickel dithiolene complexes undergo facile single-electron reductions leading to the formation of paramagnetic radical anion when singly reduced and a diamagnetic nickelate (II) when doubly reduced (Figure 3.2).



**Figure 3.2.** Redox activity of Ni dithiolene complex.

Two different situations may occur upon addition of an electron to NiTDT species (i.e. formation of  $[\text{NiTDT}]^-$ ). In the first case, electron occupies a metal d-orbital of the  $\text{M}^{\text{II}}$  ion, which is therefore reduced to  $\text{M}^{\text{I}}$  (case of an “innocent” ligand). The Multiplicity of  $[\text{NiTDT}]^{-1}$  anion containing  $\text{Ni}^{\text{I}}$  is 2. In the 2<sup>nd</sup> case, the electron fully or partially occupies an antibonding orbital of  $\text{L}^{-1}$  ligand (in case of non-innocent ligand). In this case two values of different spin states can exist: quartet and open-shell doublet. In a recent report, the magnetic susceptibilities of some synthesized systems based on NiTDT core *i.e.*, Tetrabutylammonium Bis(5-(2-thienyl)-2,3-thiophenedithiolato)-nickelate(II),  $[\text{Bu}_4\text{N}]\text{NiTDT}$  and various salts of NiTDT were measured by NMR in solution using the Evans method<sup>150, 151</sup> and also in the solid state using vibrating-sample magnetometry and the obtained susceptibility values are found to be greater than  $1.73 \mu_B$ , indicating  $S=1/2$ . Hence, all the subsequent computations on the studied complexes are performed assuming the doublet state as the ground state.

### 3.4.2. HOMO-LUMO Gap, Excitation Energies and NTOs analysis

The set of compounds we have studied can be categorized into two subsets: (a) Thiophene expanded NiTDT and its derivatives (1a, 1b, 1c; Scheme 3.1) and (b) Phenyl expanded NiTDT and its derivatives (2a, 2b, 2c; Scheme 3.1). In order to have a clear idea which orbitals are responsible for transitions, we have analyzed natural transition orbitals (NTOs). As can be seen in Figure 3.3, the HOTO (highest occupied transition orbital) of the entire studied complex (1a, 1b, 1c & 2a, 2b, 2c) are found to have comparable contribution from metal and ligand. On the contrary, the LUTO (lowest unoccupied transition orbital) is primarily composed of ligand-based orbitals. For complexes 1a, 1b and 2a, 2b, HOTO is more or less localized at the central metal dithiolene core, with some electron density dissipation onto the

pendent thiophene; whereas for complexes 1c and 2c, the HOTO is mainly constituted from the ionic donor part and the LUTO is from ionic acceptor part clearly indicating electron delocalization at ionic terminals. Hence from the transition orbital analysis it can be noticed that charge transfer takes place from one terminal to the other for zwitterionic complexes (1c, 2c).

From the comparison of HOMO and LUMO energies in these systems (Table 3.1), it can be concluded that attachment of electron donor-acceptor group ( $-\text{NH}_2$  and  $-\text{CN}$ ) in compounds 1b, 2b marginally affect the HOMO energy level, though LUMO is stabilized to some extent. However, the LUMO energies are found to be significantly reduced in zwitterionic complexes 1c and 2c, resulting decrease in HOMO–LUMO energy gap (HLG) (Table 3.1). Hence compared to the two synthesized systems (1a & 2a), all our designed systems possess lower value of HLG. Another important point to note is that both the HOMO and LUMO are oriented in mutually perpendicular fashion in 1b, whereas both the orbital lie in the plane of ring in 2b (Figure S7 in ESI).<sup>152</sup> This difference in the orientation of MOs can be correlated with their first hyperpolarizability value (Table 3.1), which is higher in 2b than 1b.

**Table 3.1.** HOMO/LUMO energies and  $\beta_{\text{tot}}$  values of NiTDT and its derivative computed in gas-phase at UB3LYP/6-311++g(d,p) level of theory.

Molecule	Energies in gas-phase (eV)			$\beta \times 10^{-30}$ esu
	HOMO <sup>a</sup>	LUMO <sup>b</sup>	$\Delta E_{\text{H-L}}$ <sup>c</sup>	
Th-NiTDT	-1.838	0.724	2.562	4.02
nTh-NiTDT	-2.002	0.056	2.058	455.92
zTh-NiTDT	-2.1284	-1.7566	0.3714	5890.9
Ph-NiTDT	-1.805	0.830	2.635	22.67
nPh-NiTDT	-1.962	0.155	2.117	643.08
zPh-NiTDT	-2.34	-1.6587	0.6813	18553.6

<sup>a</sup>HOMO stands for highest occupied molecular orbital.

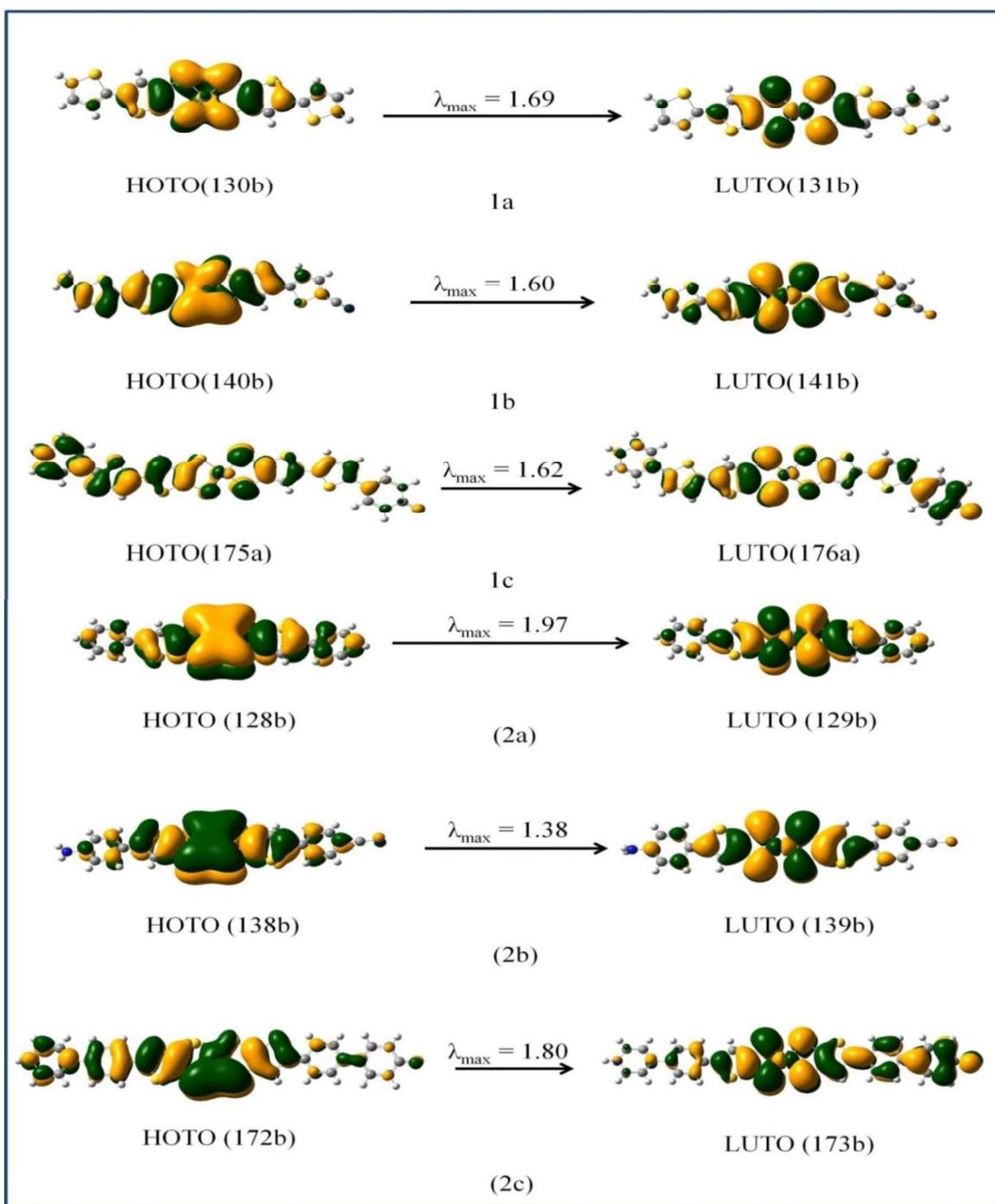
<sup>b</sup>LUMO stands for lowest unoccupied molecular orbital.

<sup>c</sup> $\Delta E_{\text{H-L}}$  represents HOMO-LUMO energy gap.

**Table 3.2.** TDDFT calculated transitions for Thienyl (1a) and Phenyl (2a) expanded analogues of NiTDT core and its derivative (1b, 1c & 2b, 2c) at CAM-B3LYP/6-311g(d,p) level of theory.

Compound	$\lambda_{\max}^{\text{cal}}$ (nm)	$f$	Primary description
1a	1173	0.2274	130B to 131B
1b	1229	0.1749	140B to 141B
1c	1371	0.6975	175A to 176A
2a	1103	0.2589	128B to 129B
2b	1057	0.2089	138B to 139B
2c	1414	0.3635	172B to 173B

In order to explain the variation of optical properties in NiTDT series, the electronic excitation energies of the monoanions (1a and 2a) are calculated using TDDFT approach and compared with the experimental data. The  $\lambda_{\max}$  values for 1a and 2a have been calculated as 1438 nm and 1281 nm, which are in reasonable range to the experimentally measured values (1108 and 1076 nm).<sup>115</sup> However, the absorption wavelengths (1173 and 1103 nm) when calculated in the gas phase, much closer result compared to the solution phase has been obtained. Thus for the designed systems gas phase only calculations are performed to get the absorption wavelength. For subset 1a, 1b, 1c and 2a, 2b, 2c, excitation energy and HLG follow the same trend (Table 3.2) as explained earlier that the donor-acceptor group decrease the HLG consequently increases the absorption wavelength. There is only one exception, the excitation energy of 2b which is more than 2a. The excitation of the Ni derivatives is an intramolecular charge transfer ( $\pi$ - $\pi^*$ ) over the  $\pi$ -type orbitals of the ligand.



**Figure 3.3.** The dominant natural transition orbital (NTO) pairs for the systems under study. The “hole” (highest occupied transition orbital; HOTO) is on the left, the “particle” (lowest unoccupied transition orbital; LUTO) on the right. The associate eigenvalues,  $\lambda_{\max}$  is given over the arrow.

### 3.4.3. NLO Properties

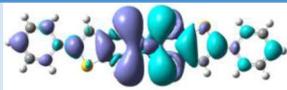
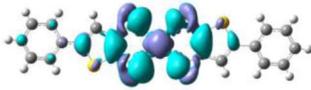
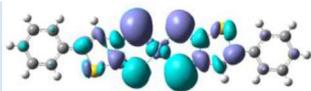
From the reported values in Table 3.1, complexes 1c and 2c with lowest HLG are found to have the highest values of  $\beta_{TOTAL}$  among the members of NiTDT series, which delineate an inversely proportional relation between the HLG and intrinsic first hyperpolarizability.<sup>153, 154</sup> To explain the origin and variation of NLO responses in NiTDT series, the  $\beta$  densities and transition dipole moments (TDM) are also calculated for these systems under investigations. Table 3.3 shows three strong absorption peaks with their oscillator strength ( $f$ ) and pictorial presentation of transition dipole moments (TDM) for the corresponding transition for system 2a. These data are also in agreement with the fact that the oscillator strength ( $f$ ) is directly related to the square of the TDM (in atomic unit),  $f = \frac{2}{3} \Delta E \times (D_x^2 + D_y^2 + D_z^2)$ , where  $\Delta E$  denotes the transition energy between the two states. From the reported TDM plot in Table 3.3, we can also observe that for energy state ( $S_4$ ) with highest oscillator strength, the electrons from one terminal is transferred to the other terminal. For the same system (2a), when we consider the energy states with lower oscillator strength ( $f$ ) values (e.g. states  $S_7$  and  $S_9$  in Table 3.3), the transitions are referred to as local excitations indicating electron oscillation of the state  $S_4$  is the strongest. Keeping the previous observations in mind, the transitions with highest oscillator strength for each of the remaining systems have been considered. The results are reported in Table 3.4 along with a pictorial presentation of the transition dipole moment in Figure 3.4. For subset 1a, 1b, 1c, highest value of TDM has been found for 1c which can be evident from their highest  $\Delta r$  index value.<sup>155</sup> This index is introduced with the aim of exploring the metric of excited electronic states in the framework of the time-dependent density functional theory. It is based on the charge centroids of the orbitals involved in the excitations and can be interpreted in term of the hole-electron distance. It has been reported in the literature that the type of excitation can be judged with the help of this index.  $\Delta r \leq 1.5 \text{ \AA}$  indicates local excitations, whereas  $\Delta r \geq 2.0 \text{ \AA}$  indicates long-range excitations.<sup>155</sup> Theoretical predictions can also be outlined here. The hole-particle pair interactions could be related to the distance covered during the excitations, so one possible descriptor could be their average distance, weighted in function of the excitation coefficients. The following definition will be then introduced:

$$\Delta r = \frac{\sum_{i,l} (K_i^l)^2 \left| \langle \varphi_i | r | \varphi_l \rangle - \langle \varphi_l | r | \varphi_i \rangle \right|}{\sum_{i,l} (K_i^l)^2} \quad (3.7)$$

where index  $i$  and  $l$  run over all occupied and virtual MOs, respectively.  $\varphi$  is orbital wave function.

For 1c, the electrons from donor part are transferred to the acceptor part with strongest electron oscillation amongst this set. We found similar observation for the next subset. Hence a nice correlation between  $\Delta r$  index, TDM and first hyperpolarizability has been found. In a nutshell ionic donor-acceptor group can increase the TDM as well as first hyperpolarizability values to a large extent.

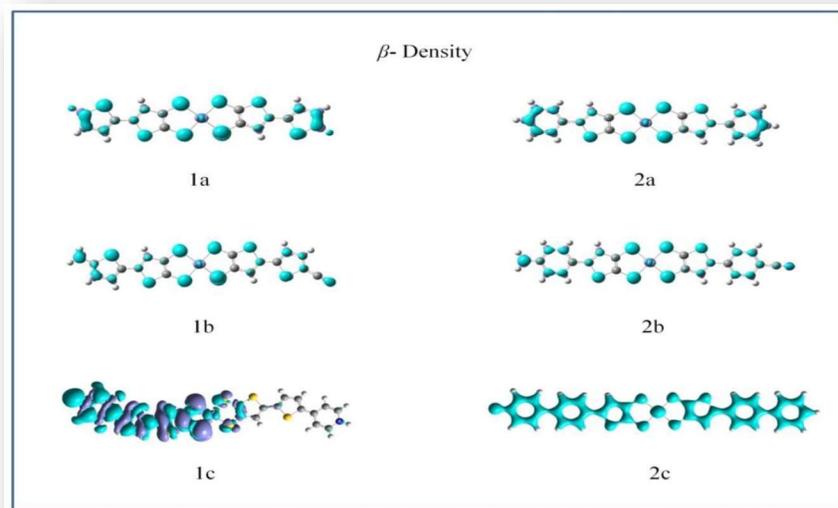
**Table 3.3.** Transition energies (eV, nm), their oscillator strengths ( $f$ ) and transition dipole moment densities for three strong transitions for Ph-NiTDT. The purple color implies charge increase upon excitation and the turquoise color implies charge depletion. The isovalue is  $4 \times 10^{-4}$  in a.u.

Energy State	eV	nm	$f$	Transition dipole moment density
S <sub>4</sub>	1.1238	1103.25	0.2589	
S <sub>7</sub>	1.6836	736.44	0.0138	
S <sub>9</sub>	1.9185	646.25	0.02	

**Table 3.4.** Major transition energies (eV, nm), their oscillator strengths ( $f$ ),  $\Delta r$  index and eigenvalues for three strong transitions for two sets of complexes (1a, 1b, 1c & 2a, 2b, 2c) calculated at CAM-B3LYP/6-311g(d,p).

Complex	State	nm	$f$	$\Delta r$ (Å)	Primary description, Eigenvalues ( $\lambda_{\max}$ )
1a	S <sub>4</sub>	1103	0.2589	0.36	128b-129b, 1.97
1b	S <sub>5</sub>	1057	0.2089	1.40	138b-139b, 1.38
1c	S <sub>1</sub>	1414	0.3635	8.60	172b-173b, 1.80
2a	S <sub>5</sub>	1173	0.2274	0.33	130b-131b, 1.69
2b	S <sub>4</sub>	1229	0.1749	0.87	140b-141b, 1.60
2c	S <sub>5</sub>	1371	0.6975	6.51	175a-176a, 1.62





**Figure 3.5.** *Isosurfaces of the static  $\beta$  density of all the studied complexes calculated at UB3LYP/6-311++g(d,p) level.*

### 3. 5. Conclusions

In the present computational study, the nonlinear optical properties of two synthesized systems, phenyl expanded and thienyl expanded thiophene fused nickel dithiolenes have been studied. Both the systems possess very low value of first hyperpolarizability. We systematically modify their structures by substituting neutral and zwitterionic donor-acceptor group at the aryl (phenyl and thienyl) ring to have high NLO response. After careful inspection of the HOMO-LUMO energies of all the six systems, we noticed that neutral donor-acceptor group marginally affects the HOMO energy level, whereas the LUMO is stabilized to some extent. Hence HOMO-LUMO energy gap (HLG) decrease. However LUMO energies are found to be significantly reduced for the zwitterionic complexes resulting large decrease in the HOMO-LUMO energy gap. Hence, HLG gradually decreases from neutral to ionic substituents for both sets of the designed systems. This observation has also been supported by the excitation energy calculations with TDDFT approach. From the calculated first hyperpolarizability values, it has been noted that the zwitterionic compounds possess very large values of  $\beta$  with low HLG. We find that by substituting ionic groups at the two ends of the Ni complex, the  $\beta$  values enhanced by at least 10-15 times than that of the molecules without any such substituent. By systematic analysis, a nice correlation between  $\Delta r$  index, TDM and  $\beta$  value have been observed. We anticipated that if synthesized, these molecules may prove to be useful in optical uses.