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Theoretical Study on Charge Transport of Dithiolene Nickel Complexes

Vu Thi Thu Huong, Truong Ba Tai* and Minh Tho Nguyen*

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Organic semiconducting materials play animportant role in the fabrication of high performance organic electronic devices. In the present work, we theoretically designed a series of organic semiconductors based on nickel complexes. Their characteristics of charge transport were investigated using DFT computational approaches. Based on computed results, all compounds designed are found to be excellent candidates for ambipolar organic semiconductors with low reorganization energies for both hole and electron. The (*I-V*) characteristics and transmission spectra of materials show that replacement of benzene rings by thiophene rings results in an increase of their HOMO and LUMO energy levels. HOMOs of compounds containing thiophene end-groups are likely dominant for their conductance, while LUMOs of compounds containing benzene end-groups mainly affect their conductance. The electron distribution in these frontier MOs is identified as the main reason which makes the conductance of the compounds in first series higher than those of the laters, respectively.

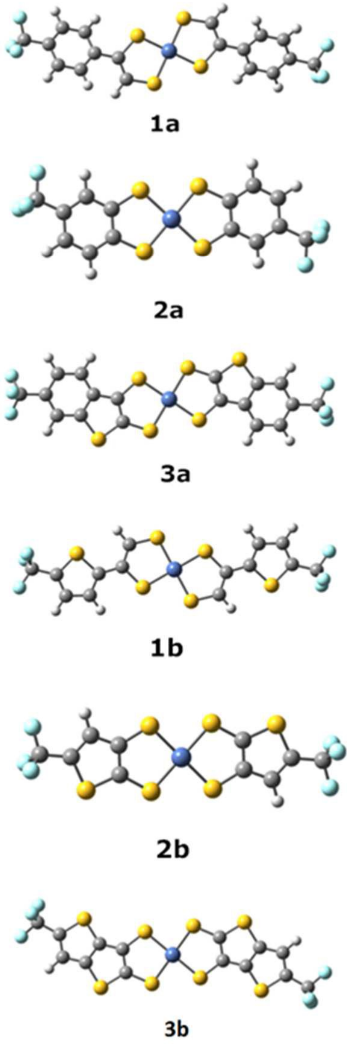
Introduction

Designing and developing new organic semiconducting materials have greatly been attractive to scientists over several past decades in part due to their important role in the fabrication of high-performance organic electronic devices. While a large number of molecular and polymeric species have experimentally and theoretically been found as good materials for p-type semiconducting materials,[1,2,3,4] only a limited number of compounds belonging to n-type materials have successfully been developed.[5,6] Of the numerous organic molecules explored, the complexes containing transition metals linked to bis-dithiolene moieties are intriguing species since they possess low LUMO levels, which is a necessary condition to obtain a good charge transport characteristic for n-type semiconducting materials.

In fact, transition metal bis-dithiolene compounds were explored as early as 1970s, and most studies were only concentrated on their structures, bonding and activities. Their applications in biological area and especially in molecular materials have been extensively investigated due to their diverse physical properties such as optics, magnetism, and superconductivity.[7,8,9,10,11,12]

Nickel dithiolene complex were first reported in 1994 to have mobility in a range of from 10^{-3} to 10^{-5} $cm^2V^{-1}s^{-1}$.[13] Subsequently, many derivatives were studied for use as molecular semiconductors. For instance, the high electron mobility of 3.8 x 10^{-2} $cm^2V^{-1}s^{-1}$ was found for Ni bi(o-diiminino-benzo-semiquinoate) compounds[14] and methyl-substituted derivatives.[15] The bis(dithiobenzyl) nickel and bis(4-di-methylaminodithiobenzyl)nickel were suggested as good n-type organic semiconductors with electron mobility in the range of $3.0x10^{-6}$-$2.0x10^{-5}$$cm^2V^{-1}s^{-1}$ and 10^{-4}-10^{-3} $cm^2V^{-1}s^{-1}$, respectively.[16,17] The latter was reported as a good ambipolar organic semiconductor with high air stability.[17] Some theoretical studies on Ni-complexes for molecular electrics were recently reported.[18,19,20] The electronic properties of many other nickel complexes were summarized in a recent review by Anyfantis and co-workers.[21] It is surprising that while a large amount of experimental studies were carried out on these intriguing systems, theoretical investigations are so scare. Theoretical explorations at molecular level are not only useful for a better understanding of the effects of chemical structures and interaction between materials and electrodes to the characteristics of charge transport, but they also give us the tool in designing new effective materials with potentially low cost.[22]

In this context, we carried out in the present work theoretical investigations on two series of nickel complexes **1a-3a** and **1b-3b** containing Ni-bi-(dithiolene) core, and trifuoromethyl as terminal groups (Fig. 1). In fact, compound **1a** which was experimentally synthesized was found to be a good n-type semiconductor with an electron mobility of 0.11 $cm^2V^{-1}s^{-1}$, on/off ratio of $2x10^6$ and exhibit good air stability.[23] The compound **2a** has a chemical structure similar to **1a**, but benzene rings are fused to increase the planarity feature of molecule. To consider the effects of conjugated length on the charge transport characteristics, the compound **3a** is designed by adding one excess thiophene ring into each size of compound **2a**. It was known that replacement of benzene rings by heterocycles such as thiophene tends to increase the air stability for molecules.[24,25] Additionally, thiophene-based compounds usually have high-packing crystallized structure in the solid state, that are very important property to achieve effective charge transport.[26,27] Therefore, the compounds **1b**-**3b** are designed by simply replacing the benzene ring in **1a**-**3a** by thiophene ring.



1a

2a

3a

1b

2b

3b

Fig. 1 Geometries of compounds **1a**-**3a** and **1b**-**3b** (PBE/6-31G(d,p))

Our theoretical predictions interestingly show that the compounds designed in such a way can be used as excellent candidates for ambipolar organic semiconductors having low reorganization energies (0.23 eV - 0.30 eV for electron and 0.06 eV -0.25 eV for hole) and high conductance.

Computational Methods

Geometrical optimizations and calculations of harmonic vibrational frequencies of all complexes considered **1a**-**3a** and **1b**-**3b** at the neutral, anionic and cationic states are performed using density functional theory with the PBEPBE functional,[28] in conjunction with the 6-31G(d,p) basis set.[29] This functional was proven in recent studies to be effective enough to determine the geometries of transition metal complexes.[30,31]

The nickel complexes were reported to be diradicals in which open shell singlet state is usually more stable than closed shell singlet state.[32,33,34,35] Therefore, we performed the test of stability of the electronic structure for all compounds **1a**-**3a** and **1b**-**3b** at neutral, cationic and anionic states by applying symmetry broken DFT solution. This was done by means of stability analysis of the DFT solution, which is similar to the test for stability of Hartree-Fock wavefunctions (as carried out using the Gaussian keyword STABLE=OPT[36,37]). To further confirm our calculations, all compounds at neutral state were re-optimized using a mixing of the initial orbital guess which allows us to detect any open-shell singlet configurations.

The reduction and oxidization potentials of the compounds considered in solution are calculated by using a protocol recently developed by Davis and Fry.[38] Firstly, optimizations of geometries and calculations of vibrational frequencies of each compound in the neutral, anionic and cationic charge states are performed using the B3LYP functional[39] along with the 6-31G(d,p) basis set. Single point electronic energies are then obtained using a larger basis set (B3LYP/6-311++G(2df,2p)). Addition of a set of diffuse functions in the basis set is necessary to describe the structures of the anions involved in the evaluation. The SMD/IEF-PCM solvation model[40] in acetonitrile solvent is used to probe the solvent effects. These methods were demonstrated to be effective to obtain the reduction and oxidation potentials of PHA compounds,[41] as well as phenylene and thiophene oligomers[42] in solution.

The absolute potentials at 298K are obtained using the following equation (1):

$$E^{298}{}_{\mathrm{Abs}} = E^{289}{}_{\mathrm{calc}} - 0.03766 \qquad (1)$$

where $\mathrm{E}^{298}{}_{\mathrm{calc}}$ is the difference in free energy (G) at 298K between the couples neutral/cation and anion/neutral. The value of 0.03766 accounts to small thermal correction for a free electron at 298K.[43] The reduction potential is predicted in MeCN solution for ferrocene-ferrocenium (Fc/Fc$^+$), and the standard redox couple are calculated by using the expressions (2) and (3):

Reduction: $\mathrm{E}_{1/2}{}^{298} = 1.056E^{298}{}_{\mathrm{Abs}} - 4.90$ (2)

Oxidation: $\mathrm{E}_{1/2}{}^{298} = 0.932E^{298}{}_{\mathrm{Abs}} - 3.94$ (3)

These equations were produced on basis of fitting the experimental and theoretical values of reduction and oxidation potentials of polycyclic compounds.[38]
The estimation of the HOMO and LUMO energies can be calculated as:

$$\mathrm{E}_{\mathrm{LUMO}} = E_{1/2}^{red} + 4.8 \text{ (eV), and}$$

$$E_{HOMO} = E^{oxd}_{1/2} + 4.8\ (eV).$$

Table 1 Oxidation and reduction potentials and energy levels of HOMO and LUMO of compounds in acetonitrile solution and in gas phases in units of eV

	HOMO			LUMO			$E^{red}_{1/2}$	$E^{oxd}_{1/2}$
	B3LYP (S)[a]	B3LYP (G)[b]	PBE (G)[b]	B3LYP (S)[a]	B3LYP (G)[b]	PBE (G)[b]		
1a	-6.11	-6.10	-5.33	-4.58	-4.24	-4.47	-0.22	1.31
2a	-6.71	-6.64	-5.33	-5.12	-4.69	-4.88	0.32	1.91
3a	-5.93	-6.04	-5.28	-4.59	-4.39	-4.57	-0.21	1.13
1b	-6.08	-5.97	-5.31	-4.68	-4.30	-4.50	-0.12	1.28
2b	-6.43	-6.39	-5.39	-4.90	-4.57	-4.73	0.10	1.63
3b	-5.87	-6.00	-5.24	-4.65	-4.41	-4.56	-0.15	1.07

[a] Values calculated in solution model

[b] Values calculated in gas phase

All these electronic structure calculations were carried out using the Gaussian 09[44] suite of programs.

Characteristics of charge transport of organic semiconductors do not only depend on intrinsic properties of the molecules considered,[45] their energy band gap,[46,47,48,49] and molecular conformation,[50,51,52] but are also affected by the working electrodes,[53,54] and the contact geometry of molecule-electrode interface.[55,56,57,58] In this study, the characteristics of charge transport of all complexes **1a**-**3a** and **1b**-**3b** are further investigated by using the non-equilibrium Green's function/density functional theory (NEGF-DFT) approach which is implemented in the SIESTA package.[59]

As shown in Fig. 2, a molecule was embedded in a unit cell with periodic boundary condition which consists of three parts: the left electrode, the scattering region and the right electrodes. The extended molecule contains an optimized molecular structure associated with five 4x4 Au-layers, two Au-layers at left electrode and three Au-layers at right electrode. This construction allows the periodicity of system to be maintained. Each of left and right electrodes contains three 4x4 Au-layers.

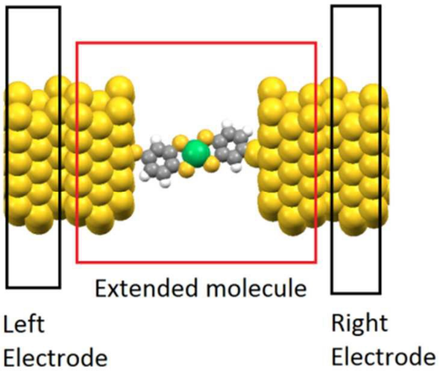


Fig.2 Computational model for a molecular junction

The modelled molecules are firstly constructed by replacing -CF_3 groups in all compounds with –SH groups, and all these are optimized at the PBE/6-31G(d,p) level. The optimized structures are then bonded to Au(111) electrodes via terminal sulfur atoms since the SH groups will lose their hydrogen atoms upon adsorption to metal surfaces. The sulfur atoms are positioned in the FCC site of Au(111) with a S-Au distance of 2.45Å from the surface. The latter value is taken on the basis of earlier studies of dithiol molecules in gold junction.[60]

Structural relaxation and all calculations of charge transport characteristics of systems are carried out using density functional theory with the GGA-PBE functional. This functional is commonly used in the literature to investigate the configurations and charge transport characteristics of molecular junction systems, and is proven to yield results comparable to experiment.[18,19,61,62] Au and Ni atomic orbitals are described using single-zeta polarized orbitals, while other atoms are described using double-zeta polarized orbitals. All systems are relaxed using a 3x3 Monkhorst-Pack grid and a 250 Ry real-space cutoff until the forces on all molecules are smaller the value of 0.04 eV/Å. Subsequently, transmission calculations are performed using the package TranSIESTA.[63] The transmission spectra and (*I*-*V*) characteristics are calculated with a 6x6 sampling of the transverse Brillouin zone.

Results and Discussion

Geometries of compounds considered.

Geometry optimizations and subsequent calculations of harmonic vibrational frequencies of all compounds considered are performed using the PBEPBE functional in conjunction with the polarized 6-31G(d,p) basis set. Shapes of all compounds considered are given in Figure 1, while their optimized structures are depicted in Figure S1 of the Supplementary Information (ESI) file. Among all six compounds examined in our study, **1a** is the only one which was studied in experiment.[21] The computed Ni-S and C-S bond lengths **1a** are equal to 2.13 and 1.73Å, respectively, which agree well with experimental data of 2.11-2.14 and 1.68-1.73Å.[23] Our calculations show that geometries of compound **1a**and **1b** are slightly distorted out of the molecular plane, whereas the fused compounds **2a**-**3a** and **2b**-**3b** exhibit planar structures. We expect that these planar structural characteristics result in their solid state having more packing crystallization structures, which subsequently improve their charge mobility in solid state. In the cationic state, the cations **1a**$^+$ and **1b**$^+$ also have distorted geometries, while the cations **2a**$^+$, **2b**$^+$, **3a**$^+$ and **3b**$^+$ almost retain the planar form. Following attachment of one excess electron, geometries of all anions **1a**$^-$-**3a**$^-$ and **1b**$^-$-**3b**$^-$ become distorted from the planarity.

Because the square planar Ni-complexes usually display a diradical character in which open-shell singlet states could be more stable than their closed-shell singlet states, a test of stability of the DFT solutions for all compounds at the neutral, cationic and anionic states are performed using the symmetry broken DFT method. The results given in Table S1 showed that except for the neutral **2a**, all DFT solutions are well stable with respect to orbital mixture. The compound **2a** exhibits a marginal diradical character as the difference in energy between its open-shell and closed-shell singlet states is negligible (ΔE =0.00003 a.u). The same results are obtained for the neutral species when we re-optimize these species allowing a mixture of the initial orbital guesses (using the option of "guess=mix" in Gaussian which allows us to detect any open shell singlet). It seems that the terminal groups $-CF_3$ considerably affect and reduce the diradical character of these molecules. To further confirm our computed results, the test of stability of waverfunctions was also carried out using the B3LYP/6-31G(d,p) level of theory which was commonly used in the previous reports.[32,33,34,64,65] Our B3LYP results are in good agreement with the PBE results that the B3LYP-DFT solutions of all compounds considered are well stable with respect to orbital mixing. The compound **2a** exhibits a tiny energy gap of 0.0005 a.u. between the open-shell and closed-shell singlet states which is marginally larger than the value obtained by using PBE functional.

Reduction and oxidation potentials of compounds in solution

Reduction and oxidation potentials, and subsequently energies of frontier molecular orbitals (FMOs), play an important role in evaluating the applicability of organic semiconductors. The energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) characterized for p- and n-type semiconductors, respectively, should be close to work function (WF) in vacuum of the electrodes in order to improve their charge transporting ability. Some common electrodes such as gold (Au, WF ~ 5.1 eV), calcium (Ca, WF ~ 2.9eV), or magnesium (Mg, WF ~ 3.68) are often used in experimental studies. In this study, the reduction and oxidation potentials and energy levels of FMOs of all molecules are calculated using both the SMD/IMF-PCM solvation model in acetonitrile solvent and in gas phase. The computed values of all compounds are given in the Table 1. Our computed results in solution show that the energy levels of |LUMO| and |HOMO| of **1a** are equal to 4.6and 6.1 eV which are in good agreement with the experimental values of 4.5 and 5.6 eV, respectively.[23] There are small differences in LUMO and HOMO energy levels between **1a** and **3a**, whereas the HOMO and LUMO of **2a** are lower than those of **1a**. A similar trend can be found for the series of compounds **1b** – **3b** in which the HOMO and LUMO values of **1b** and **3b** are close together and somewhat higher than those of **2b**. Our gas phase calculations show similar variable trends, although the HOMO/LUMO energy levels are somewhat changed. The HOMO/LUMO values obtained using the B3LYP functional in gas phase are quite close those obtained in solution. The PBE functional consistently provides HOMO-LUMO gaps smaller than those obtained from the B3LYP functional. The PBE HOMO values are higher, and PBE LUMO values are lower as compared those obtained from the B3LYP ones.

In general, although the HOMO/LUMO values are somewhat changed when different functionals are used, all compounds considered are characterized by low energy levels of LUMO, which vary in a range of -4.6 to -5.1 eV (-4.4 to -4.88 eV for PBE values). These values are close to the work function of 5.1 eV of gold electrode. Thus we expect that they can be used as good n-type semiconducting materials. The HOMO energy levels of **1a**, **3a**, **1b** and **3b** lie in the range of -5.9 to -6.1 eV (-5.3 to –5.4 eV for PBE values) and thus they can also be suggested as p-type organic semiconductors.

Reorganization energy for hole and electron

The intermolecular effects play an important role for organic electronic devices.[22] In order to evaluate the electron and hole mobilities of a molecule, we need to consider its reorganization energies for hole and electron. The reorganization energies are defined as the sum of geometrical relaxation energies when the species goes from the neutral state geometry to a charged state geometry, and vice versa. Accordingly, a molecule has high charge mobility when it has low reorganization energies. The latter can be defined as follows:[66]

$$\lambda_h = \lambda_0 + \lambda_+ = [E(M) - E^0(M)] + [E(M^+) - E^0(M^+)] \qquad (4)$$

$$\lambda_e = \lambda_0 + \lambda_- = [E(M) - E^0(M)] + [E(M^-) - E^0(M^-)] \qquad (5)$$

where λ_h and λ_e are reorganization energies for hole and electron, respectively; $E(M^+)$ and $E(M^-)$ the total energies of the cationic and anionic states with the optimized geometries of the neutral ground state, respectively; E(M) the total energy of the neutral state with the optimized geometries of the cationic species (for equation 4) and of the anionic species (for equation 5); $E^0(M)$, $E^0(M^+)$ and $E^0(M^-)$ the total energies of the neutral, cationic and anionic ground state species, respectively.

Table 2 Reorganization energies for electron and hole of compounds obtained at the PBE/6-31G(d,p) level of theory

Comp	λ_e(eV)	λ_h (eV)	Comp	λ_e (eV)	λ_h (eV)
1a	0.25	0.24	**1b**	0.23	0.22
2a	0.23	0.06	**2b**	0.30	0.10
3a	0.25	0.13	**3b**	0.26	0.18

It can be found in Table 2 that the chemical structure of a compound induces a remarkable effect in its reorganization energies for hole (λ_h). The λ_h values of compounds **2a** and **2b** amount to 0.06 and 0.10 eV, respectively, and are the lowest values as compared to the remaining compounds **1a**, **3a**, **1b** and **3b**. At the same conjugation length, compounds containing fused thiophene rings **3a** and **3b** contain much lower reorganization energies for hole than those of **1a** and **1b**, respectively.

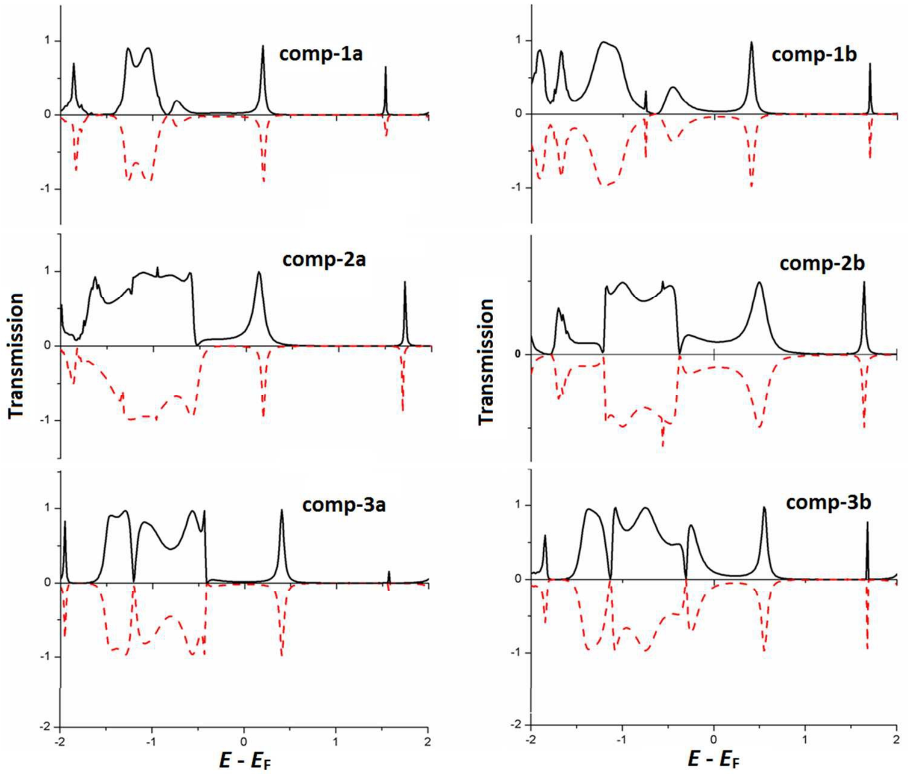


Fig. 3 Equilibrium transmission versus energy characteristics of the molecular junction. The red lines indicate the spin down transmission and the black lines correspond to the spin up

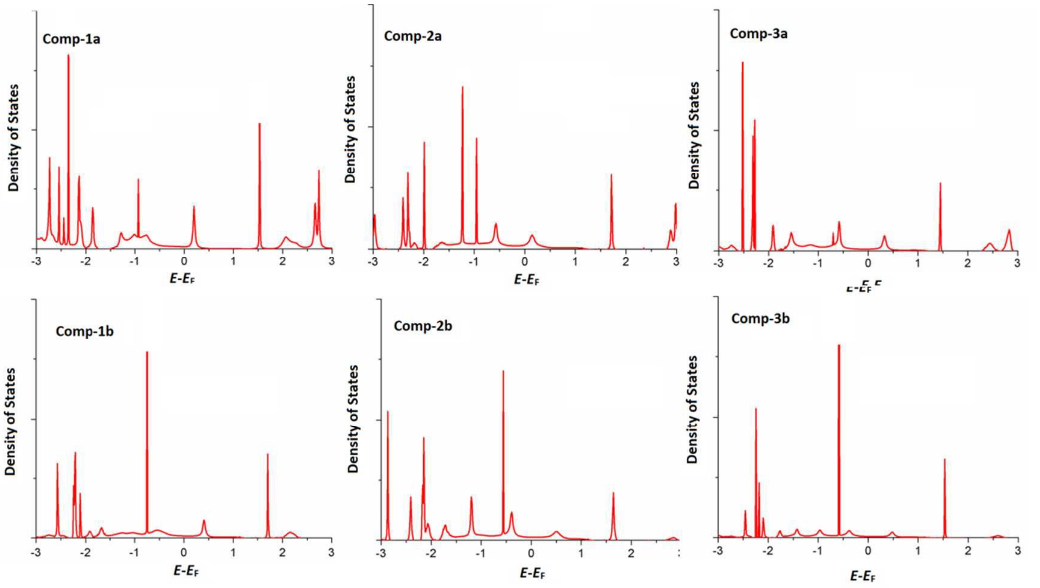


Fig.4 Density of states (DOS) for central regions of conjunction systems

The compound **3a** has the λ_h value of 0.13 eV which is lower than that of 0.24 eV of **1a**. Similarly, the λ_h value of **3b** is 0.18 eV and is marginally lower than the value of 0.22 eV of the **1b** (being the same upon rounding off). It is interesting to note that replacement of the phenyl rings in the series of **1a-3a** by the thiophene rings in series of **1b-3b** exerts a quite small effect on their reorganization energies.

Our calculations point out that the reorganization energies for electron (λ_e) of the compounds considered are quite close to each other. The λ_e values of **1a**-**3a** are basically the same, varying in the range of 0.23 to 0.25 eV. Similarly, the λ_e values of **1b**-**3b** are found in the range of 0.23-0.30 eV. These values are comparable to that of 0.23 eV of perfluropentacene (PF-PEN),[67] which is a well-known n-type semiconductor. In addition, let us again note that **1a** was found to be as a good n-type organic semiconductor in a recent experimental study.[23] We can thus expect that all novel compounds considered here can be regarded as good candidates for n-type semiconducting materials.

Although the computed HOMO energy levels of **2a** and **2b** are somewhat high, their λ_h values (0.06 eV for **2a** and 0.10 eV for **2b**) are remarkably low, even as compared to the λ_h value of 0.095 eV of pentacene which is a typical p-type semiconductor. The λ_h values of **3a** and **3b** are somewhat higher, but they are still quite low in comparison to those of known p-type semiconducting materials. Thus we would suggest that the novel compounds **2a**, **2b**, **3a** and **3b** can also be used, if experimentally prepared, as p-type organic semiconductors.

I-V characteristics

To obtain a better understanding about the charge transport characteristics of molecules considered, and to further explore their applications in molecular electronic devices, the conjugation systems of the modelled molecules are now examined. It is worthy to note that for applications in the organic electronic devices, both intermolecular effects and molecule-electrode interfaces plays more important role.

One of the most important aims in molecular electronics is to advance the understanding of electron transport through molecules. The most common method used to attach molecules to external electrodes is to use thiolate bonds with Au(111) surfaces as external electrodes. The modelled molecules in the present work were constructed by replacing -CF_3 groups in all compounds were replaced with –SH groups and all these were optimized at the PBE/6-31G(d,p) level of theory. These extended aromatic compounds are π type conductors in which thiol end groups contact gold electrodes in our systems. More detail in computational methods can be found in the section of computational methods. This investigation allows us to understand how chemical structures of molecules effect on their conduction in specific electrodes.

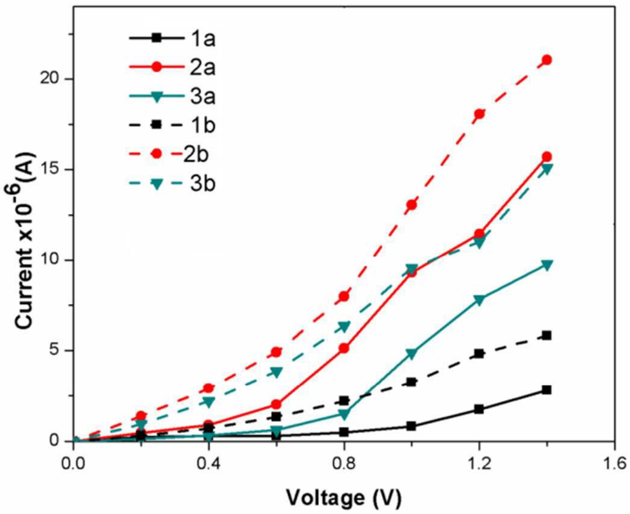


Fig. 5 *I-V* characteristics for all compounds considered.

In the series of **1a**-**3a**, the geometry of **1a** is distorted from planarity, while **2a** and **3a** have planar structure. Such structural distortion of **1a** decreases its electron conjugation due to a reduced orbital overlap between aromatic rings. Thus we can expect that both **2a** and **3a** have higher conductance. Earlier studies showed that the twisting of middle benzene rings in oligophenylenes considerably reduces their conductance.[68]

The zero bias transmission spectra of modelled structures are depicted in Fig. 3, whereas their *I-V* characteristics are showed in Fig. 5. The transmission spectra of compounds are interesting subjects of the experimental measurement using scanning tunneling microscopes (STMs).[69,70] The transmission coefficient at Fermi level can be used to calculate conductance of conjunction systems and subsequently their current-voltage characteristics. In addition, the transmission spectrum can be considered as the most intuitive representation of electron transport behaviour since it shows distinct difference between the up and down spin spectra. The local peaks around Fermi level allows us to understand how the frontier molecular orbitals affect to the charge transport characteristics of systems.

The current-voltage (*I-V*) characteristic of systems that can be directly measured in experiments is considered as the primary observable allowing us to determine conductance of molecules. In theoretical NEFG+DFT approach, the current-voltage curves of molecular junctions are obtained using the Landauer-Buttiker formula[71] as follows:

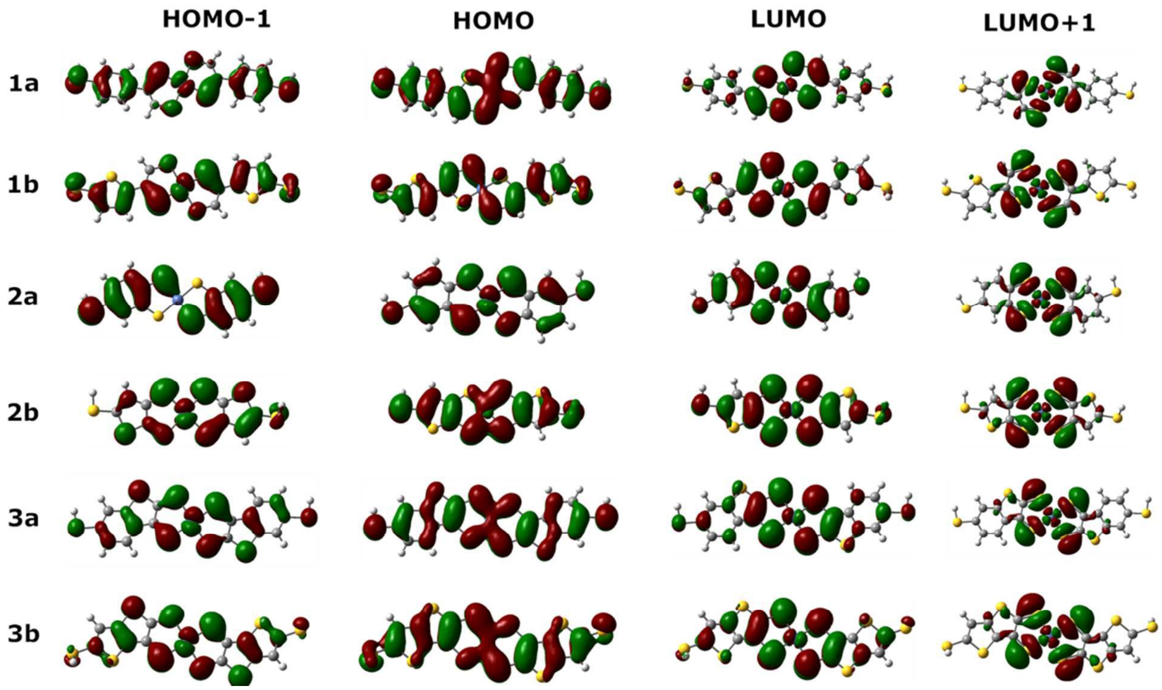


Fig. 6 Shapes of frontier molecular orbitals of **1a-3a** and **1b-3b**

$$I_\sigma(V) = \frac{e}{h}\int T_\sigma(E,V)[f(E-\mu_L) - f(E-\mu_R)]dE \qquad (6)$$

where $T_\sigma(E,V)$ is transmission coefficient for the spin-up/spin-down electron, and defined as

$$T_\sigma(E,V) = Tr[\Gamma_L G_\sigma \Gamma_R G_\sigma^+]$$

G_σ is the spin-dependent retarded Green's function of central scattering region, Γ_L and Γ_G are the coupling matrix between the scattering region and the left and right electrodes, respectively. $f(E-\mu_{L/R})$ is the Fermi function and μ_L and μ_R are the chemical potentials for left and right electrodes, respectively.

Our calculations show that the planar compounds containing fused rings **2a** and **3a** have higher conductance as compared to that of **1a** (Fig 3 and 5). The **2a** possesses the highest conductance, while the lowest conductance is now found for the known **1a**. At the same conjugation length, the conductance of **3a** containing fused thiophene rings turns out to be considerably higher than that of **1a.** These observations are similar to those found in the series of polyphenyls earlier reported. Ratner *et al.*[68] showed that p-benzene dithiol (PBD) exhibits the highest conductance in the series of polyphenyl dithiols, and the conductance of molecules isreduced when the chain length of the polyphenylene moiety is increased.

Similar trend is now found for the series of compounds **1b-3b** of which **2b** exhibits the highest conductance (Fig 3 and 5). The conductance of **1b** is the lowest one partly due to its distorted geometrical structure. More interestingly, although the conjugation length of both series **1a-3a** and **1b-3b** are close to each other, **1b-3b** have higher conductance as compared to those of **1a-3a**, respectively. It thus appears that the conjugation length does not affect significantly the molecular conductance. This observation is similar to that previously found for polyphenyl dithiols.[68] To gain more insights into these intriguing phenomena, we further examine their transmission spectra and electron distribution in frontier molecular orbitals.

The spin-resolved zero-bias transmission spectra predicted in Fig. 3 showed that excepting compound **2a** whose transmission spectrum is slightly asymmetrical, the transmission spectra of all compounds almost exhibit symmetry feature. This can come from the fact that the **2a** possesses diradical character, while other remaining compounds are closed shell singlet states. In addition, the Fermi levels of **1a-3a** are closer to the LUMO than to the HOMO upon contact with gold electrodes. Oppositely, the metal Fermi levels of **1b-3b** are closer to their HOMO. Similar observations can be found for the analysis of density of states (DOS). The DOS for center region of systems given in Figure 4 show the intensity local peaks which almost overlap their intensity peaks of transmission spectra. It can be seen that replacing benzene rings in **1a-3a** by thiophene rings in **1b-3b** shifted up their HOMO/LUMO energy levels as compared to the Fermi levels. Consequently, the occupied orbital (HOMO) of **1b-3b** will likely dominate their conductance, while the LUMO of **1a-3a** will mainly contribute to their conductance. The shapes of FMOs displayed in Fig. 6 emphasize that there is a good electron delocalization over the HOMOs of molecules **1b-3b** which subsequently results in their higher conductance.

For **1a-3a** whose electron density in LUMOs plays a more important role, electrons are less delocalized. Additionally, although contributions of LUMO+1 and HOMO-1 to the molecular conductance are smaller than those of LUMO and HOMO, they also affect the computed conductance values. The LUMO+1 of **1a-3a** are σ orbitals and lie far away from their LUMO in transmission spectra. Thus they almost do not give any contribution to the conductance of these molecules. On the contrary, the HOMO-1 of **1b-3b** are π orbitals and lie close to their HOMOs. As a consequence, it is expected that they will considerably take part in their high conductance. Such electron contributions can explain the lower conductance of **1a-3a** as compared to **1b-3b**.

We would like to note that the compound **1a** was experimentally synthesized.[23] The Ni-complexes containing the planar $[Ni(S2C6H4)_2]^{n-}$ species were interesting subjects in many experimental studies.[72,73] In addition, a large number of Ni-complexes containing bis-dithiophene were also synthesized and their physicochemical properties were presented.[21] Thus we expect that the compounds **2a-3a** and **1b-3b** will be promising subjects for experimental studies in near future.

Conclusions

In this theoretical study, we designed and investigated the characteristics of charge transport of a series of organic semiconductor based on nickel complexes using DFT methods. Of particular interest, our results showed that all compounds **1a-3a** and **1b-3b** behave as, if they could be all prepared, excellent candidates for ambipolar organic semiconductors with low reorganization energies for both hole and electron. The planar compounds containing fused rings such as **2a-3a** and **2b-3b** exhibit lower reorganization energies for hole as compared to the **1a** and **1b**. Their reorganization energies for electron are comparable due to geometrical distortion of anions.

The (*I-V*) characteristics and transmission spectra of materials showed that replacement of benzene rings in **1a-3a** by thiophene rings in **1b-3b** results in an increase of their HOMO and LUMO energy levels. The HOMOs of **1b-3b** have thus likely a dominant contribution to their conductance because they lie closer to the Fermi energy level than their LUMO counterparts. The LUMOs of compounds **1a-3a** mainly contribute to their conductance. Electron distributions in these frontier molecular orbitals are identified as the main factor which makes the conductance of **1b-3b** higher than those of **1a-3a**, respectively.

Because the compound **1a** was recently synthesized, and also effectively used as a good n-type semiconducting material in experimental study, we would hope that our present theoretical results strongly stimulate the experimental investigations in near future in the use of nickel complexes for these applications.

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Department of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium.
E-mails: truong.batai@chem.kuleuven.be and minh.nguyen@chem.kuleuven.be

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