



Computational studies of hole/electron transport in positional isomers of linear oligo-thienoacenes: Evaluation of internal reorganization energies using density functional theory



Anup Thomas^{a,*}, Ramesh Kumar Chitumalla^b, Avinash L. Puyad^c, K.V. Mohan^a, Joonkyung Jang^b

^a Center for Computational Research in Clean Energy Technologies (CCRCE), Sree Chitra Thirunal College of Engineering (SCTCE), Pappanamcode, Trivandrum, Kerala 695018, India

^b Department of Nanoenergy Engineering, Pusan National University, Busan 609-735, Republic of Korea

^c School of Chemical Sciences, Swami Ramanand Teerth Marathwada University, Nanded 431 606, MS, India

ARTICLE INFO

Article history:

Received 4 January 2016

Received in revised form 22 March 2016

Accepted 2 May 2016

Available online 4 May 2016

Keywords:

Hole transport

Electron transport

Reorganization energy

DFT/TDDFT

ABSTRACT

The paper computationally investigates and compares the internal reorganization energies associated with the intermolecular transport of a hole and electron in a series of positional isomers of fused planar acenodithiophenes (**S(n)a-c**) with those of linear acenes (**LA(n)**). In particular, it is observed that, amongst the positional isomers, the para isomers (**S(n)c**) have got ultra-small reorganization energies than the other two positional isomers. The non-bonding character of frontier molecular orbitals (FMO) of these para isomers is the main reason for the existence of this phenomenon. Secondly, the non-bonding character in the FMO of these molecules is mediated by their open shell singlet biradical nature in ground state, as revealed by the Spin-flip time dependent density functional theory analysis. These aforementioned findings and characteristics of **S(n)c** series of molecules, strongly recommend that these molecules if synthesized will show high charge carrier mobility. Also we have revealed that biradicaloid nature of a molecule is new interesting design factor to achieve low reorganization energies.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Semiconducting organic π -conjugated materials are active elements in organic light-emitting devices (OLED), organic field effect transistors (OFET), organic thin film transistors (OTFT), and photovoltaic cells. The advantages of organic components over standard/existing inorganic materials are: lower costs, lighter weights, easier fabrication, malleability and tuning of properties to high resolutions through suitable substitutions [1–5]. These attractive features propelled governments and industrialists to invest heavily toward the research and development of organic electronics. This has led not only to innovations in the material domain – through inventions of efficient devices – but also toward a much more nuanced theoretical understanding of their intermolecular interactions, properties due to substitutions, geometry, packing of the molecules in the solid state – to name but a few [5]. One significant contribution of these researches has been to show how the optoelectronic applicability of such materials depends on various factors such as: alignment of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), energy

levels for the charge carrier injection from the electrodes, and their geometrical arrangement in the solid state [1–6]. Thus, it follows that a proper understanding of all these molecular characteristics of the organic materials used in organic semiconductor devices is a prerequisite for the design and selection of appropriate molecules and for optimizing efficiency of these devices. Toward this aim, quantum chemical studies offers indispensable tools empowering our understanding of the optical and electronic properties of molecules from their electronic structure; thereby enabling the design of new and efficient materials [7,8].

A heuristical strategy for designing semiconducting materials is appending donor and acceptor groups to a suitable core structure so as to achieve p-type (hole transport) and n-type (electron transport) mobility respectively [9,10]. That is the molecules with high electron affinity (EA) and low ionization potentials (IP) with favorable intermolecular interactions, are suitable n-type and p-type semiconductors respectively. On the flip side compared to p-type materials, fewer n-type materials have been reported [7]. A well-established strategy for achieving high electron affinity (n-type mobility) is perturbing the sp^2 hybridized $-CH-$ part of the fused acene rings with hetero atoms like nitrogen [7]. It is also reported that perfluorination of fused aromatics increase the EA and hence electron mobility.

* Corresponding author.

E-mail address: anupthomas@gmail.com (A. Thomas).

To date, a large number of organic materials having semiconducting properties have been investigated. Computational studies – especially with its extensive work on organic π -conjugated materials – contribution to the field has been immense as it has proved beyond doubt the stability between theoretically determined molecular properties, experimentally observed charge carrier mobilities and their resultant performance in devices. These researches establishing the relationship between the three realms – theory, experiment and practice – has provided researchers with enormous amount of data enabling hypothezization of many structure activity relationships. The significance of computational studies – as proved in the case of organic conjugated compounds – lies precisely here: it can be used for predicting the behavior of less known or unexplored molecules.

However, a propitious discovery of recent research has been the emergence of derivatives of linear poly-acenes and fused heteroaromatics as promising materials for organic semiconductor technology [7–14]. This, pertaining to the fact that their fused structures leads to stabilized HOMO and favorable intermolecular π - π overlap: requisite factors for the optimum performance of these devices. While aceneothiophenes and oligoacenes based organic semiconductors in high performing OFETs possess mobilities higher than $1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [7,8,14]; the thiophene analogues have excellent air stability and high charge carrier mobility over linear oligoacenes [14]. Here, a systematic investigation of positional isomers of linear oligo-thienoacenes using density functional theory, (DFT) would enable a profound understanding of the electronic structure of these molecules. These results can then be used to compare these molecules with the already well researched linear oligoacenes deemed to be promising semiconducting materials. With this question in mind, the molecules oligo-thienoacenes chosen for this study are positional isomers of dithienoacene (**S2a–c**) benzodithiophene (**S3a–c**), naphthodithiophene (**S4a–c**), anthradithiophene (**S5a–c**) and tetracenodithiophene (**S6a–c**). Additionally the oligoacenes from naphthalene to hexacene (**LA2–6**) were also studied. These latter molecules have already been reported using different levels of theory here for sake of uniformity in comparison; these molecules have been studied again with the methodology used in this work. (The numbering **2–6** represents the number of fused rings in the corresponding system.) **Figs. 1 and 2** depict the 2-dimensional structures of the molecules discussed in this study.

The computational method is used to investigate twenty molecules (**Figs. 1 and 2**) to obtain a detailed picture-at the molecular level – of their: (1) molecular orbitals (HOMO and LUMO), (2) energy levels and (3) reorganization energies (*vide infra*). The main objective is to predict the behavior of **S(n)c** series relative to the oligoacenes, **S(n)a** and **S(n)b** series. To the best of our knowledge, such a detailed analysis and comparison of the electronic structures of these systems has not been carried out previously. As the molecular stacking patterns (crystal structures) are not available for most of the molecules considered here, we could not investigate certain other important parameters such as their intermolecular interactions and electronic coupling.

2. Computational details

2.1. Computation of charge carrier transport property

The charge carrier mobility of organic materials can be explained either using the band theory or the Marcus' hopping model [15]. The hopping model is more suitable when the coupling between neighboring molecules in the bulk solid is minimal. According to this model, at the molecular level, the electron/hole transport process in the thin films is the electron/hole transfer reactions between the neighboring molecules [15–18].



Here **A** represents a neutral molecule interacting with a neighboring oxidized or reduced species **A**^[+/-]. The rate constant for electron/hole transfer can be obtained from the Marcus theory [19] in an Arrhenius-like form,

$$K_{et} = \frac{2\pi t^2}{h} \sqrt{\frac{\pi}{\lambda_{\pm} k_B T}} \exp\left(-\frac{\lambda_{\pm}}{4k_B T}\right) \quad (2)$$

where **t** is the transfer integral/coupling matrix element between neighboring molecules, λ_{\pm} the reorganization energy, k_B the Boltzmann constant and **T** the absolute temperature. For competent performance, materials should have low reorganization energies and good coupling between neighbors. An evaluation of **t** would require the knowledge of relative positions of the molecules in solid state (as it is related to the energy splitting of the frontier orbitals of the interacting molecules). The mobility of the electrons/holes is

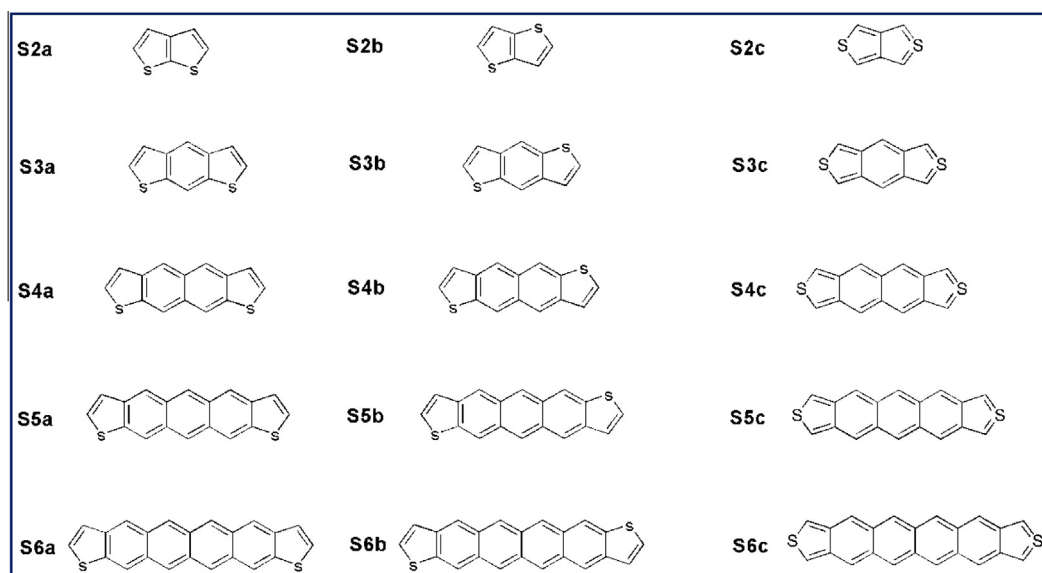


Fig. 1. Heterocyclic molecular structures of positional isomers of dithieno-acenes discussed in this work.

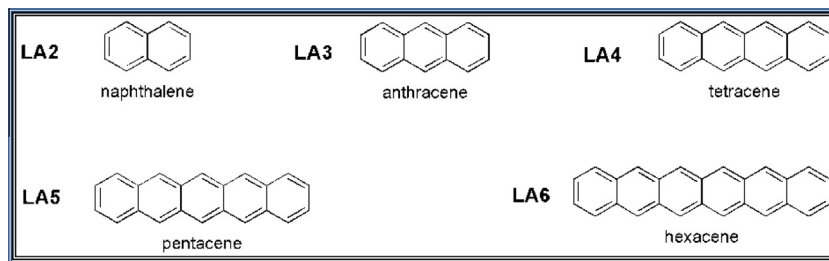


Fig. 2. Molecular structures of linear acenes discussed in this work.

predictable from the reorganization energies and in general have good agreement with the experimental observations [15–18]. Our aim here is rather to predict the reorganization energies on the basis of theoretical calculations. It is clear that, to have a larger electron/hole transport, the reorganization energies of the corresponding change from neutral to cation/neutral to anion should be low.

The reorganization energy consists of both intra-molecular contributions and polarization contributions from the surrounding environment [20,21]. The intra-molecular contribution is correlated to the geometrical changes of the molecule. Polarization contributions in organic thin films are expected to be very small and hence neglected [20,21]. Here we employ DFT methods to predict the intra-molecular reorganization energy.

The intra-molecular reorganization energies are calculated based on the model shown in Fig. 3. Here, λ_1 is the energy difference (in eV) of the positively charged molecule associated for the geometric relaxation from ground state geometry to optimized cationic state and λ_2 , the energy required to reorganize from the non-charged state at the cation geometry to the ground state upon re-accepting an electron. Total hole reorganization energies (λ_c^+) of the molecule is being obtained by adding λ_1 and λ_2 . In a similar manner, the anion reorganization energy ($\lambda_a^- = \lambda_3 + \lambda_4$) is useful in understanding the electron transport.

All the calculations discussed in this work were carried out using Gaussian09 (G09) electronic structure simulation package [22], unless otherwise specified. The molecules discussed in this work are planar and with no side group substitution, also only initial structures with high symmetry are optimized. The DFT methods employed in the work are commonly used B3LYP functional and the results obtained are compared with CAM-B3LYP and

wB97XD long range corrected (LRC) functionals. B3LYP is a global gradient corrected GGA hybrid DFT method with constant amount (25%) of Hartree–Fock HF exchange [23]. CAM-B3LYP (Coulomb attenuated version of B3LYP) and wB97XD are range separated hybrid functionals with short range (HF) exchange [24,25]. The CAM-B3LYP functional contains a fraction of 0.19 HF exchange interaction at short-range, and 0.65 HF exchange interaction at long-range [24]. For wB97XD the fraction of HF exchange at short range is 0.22 and 100% HF exchange at long range. In addition it has a dispersion correction term [25]. The range separated hybrid functionals are recommended for extended π -conjugated systems to obtain better results [26,27]. For all calculations a correlation consistent-cc-pVTZ basis set is coupled with the DFT model. The vibrational frequencies are determined at the same level to confirm the nature of stationary point. We used Q-Chem software package for the spin flip (SF) calculations [28]. The SF single point calculations have been carried out by using 50–50 functional, which is suggested for open-shell molecules [29].

3. Results and discussion

3.1. Reorganization energies

Studies on different organic systems have shown that DFT-B3LYP provides the best estimates of the geometry modifications upon ionization [5]. Reliability of B3LYP estimates of reorganization energies are validated further from the excellent agreement it shed between the experimental and simulated ultraviolet photoelectron spectroscopy UPS spectra [5,30]. The reorganization energies reported in this work are calculated using B3LYP/6-31G(d) and B3LYP/cc-pVTZ. All the neutral and oxidized/reduced states remain in the planar configuration.

The electron (hole) is localized on a single lattice site with a stabilization energy – referred to as the polaron binding energy. The polaron binding energy results from the deformations in molecular and lattice geometries that occur as the carrier localizes on a given site. The intra-molecular contributions to the polaron binding energy are equal to the geometry relaxation energy upon charging the molecule. The polaron binding energy is equal to half of the reorganization energy.

The reorganization energies λ_c^+ and λ_a^- calculated using B3LYP – of the hole and electron transfer, respectively are given in Table 1. The results obtained for LA2–LA5, S3a–S5a, and S3b–S5b are in excellent agreement with those earlier predicted by Bredas and co-workers using the B3LYP/6-31G(d,p) level theory [5]. A similar patterns can be observed through the series i.e., the reorganization energies (λ_c^+ and λ_a^-) are inversely proportional to the number of intervening fused rings. This is attributed to the increase in charge delocalization with increase in the number of fused aromatic phenyl rings [5].

For all the molecules the λ_c^+ values are less than that of the corresponding λ_a^- values. The polaron binding energy is more for

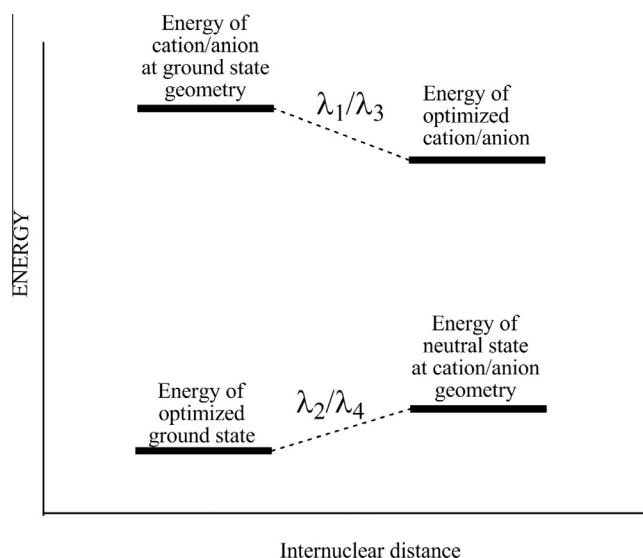


Fig. 3. Calculation of the intramolecular reorganization energy.

Table 1
Simulated reorganization energies (eV) λ_c^+ (hole transport), λ_a^- (electron transport) of all molecules along with λ_1 , λ_2 , λ_3 , and λ_4 obtained at B3LYP/cc-pVTZ level. The values given in parentheses were obtained at B3LYP/6-31G(d) level.

	λ_1	λ_2	λ_c^+	λ_3	λ_4	λ_a^-
LA2	0.095 (0.092)	0.094 (0.091)	0.188 (0.183)	0.131 (0.128)	0.131 (0.129)	0.262 (0.257)
LA3	0.071 (0.068)	0.071 (0.067)	0.141 (0.136)	0.102 (0.097)	0.102 (0.098)	0.203 (0.195)
LA4	0.058 (0.054)	0.057 (0.054)	0.115 (0.107)	0.082 (0.077)	0.082 (0.078)	0.164 (0.154)
LA5	0.048 (0.041)	0.048 (0.045)	0.097 (0.086)	0.067 (0.063)	0.067 (0.062)	0.135 (0.125)
LA6	0.041 (0.031)	0.041 (0.037)	0.082 (0.068)	0.057 (0.053)	0.056 (0.050)	0.113 (0.103)
S2a	0.068 (0.075)	0.067 (0.070)	0.135 (0.145)	0.138 (0.146)	0.132 (0.140)	0.271 (0.286)
S3a	0.052 (0.057)	0.052 (0.055)	0.103 (0.111)	0.128 (0.132)	0.127 (0.131)	0.255 (0.262)
S4a	0.049 (0.053)	0.049 (0.052)	0.098 (0.105)	0.098 (0.105)	0.098 (0.100)	0.196 (0.205)
S5a	0.047 (0.048)	0.048 (0.049)	0.095 (0.097)	0.080 (0.080)	0.080 (0.081)	0.160 (0.160)
S6a	0.046 (0.044)	0.045 (0.045)	0.090 (0.088)	0.067 (0.066)	0.067 (0.067)	0.134 (0.132)
S2b	0.199 (0.202)	0.202 (0.462)	0.401 (0.664)	0.189 (0.189)	0.185 (0.187)	0.375 (0.376)
S3b	0.084 (0.089)	0.071 (0.076)	0.155 (0.165)	0.147 (0.151)	0.145 (0.148)	0.292 (0.299)
S4b	0.052 (0.054)	0.052 (0.055)	0.103 (0.109)	0.104 (0.106)	0.105 (0.108)	0.209 (0.214)
S5b	0.049 (0.050)	0.045 (0.049)	0.094 (0.098)	0.083 (0.080)	0.079 (0.084)	0.162 (0.163)
S6b	0.044 (0.044)	0.045 (0.045)	0.089 (0.089)	0.067 (0.066)	0.067 (0.067)	0.134 (0.133)
S2c	0.032 (0.030)	0.032 (0.032)	0.065 (0.062)	0.132 (0.132)	0.129 (0.131)	0.261 (0.263)
S3c	0.021 (0.016)	0.022 (0.017)	0.042 (0.033)	0.094 (0.093)	0.094 (0.094)	0.188 (0.187)
S4c	0.019 (0.012)	0.017 (0.013)	0.036 (0.025)	0.072 (0.070)	0.070 (0.072)	0.142 (0.142)
S5c	0.016 (0.009)	0.017 (0.010)	0.033 (0.020)	0.058 (0.054)	0.059 (0.054)	0.116 (0.108)
S6c	0.014 (0.008)	0.015 (0.009)	0.029 (0.016)	0.049 (0.043)	0.048 (0.043)	0.098 (0.086)

electrons than for holes. The reorganization energies reveal that all molecules considered in this work are relatively better hole transporting (p-type) materials. The λ_c^+ values for linear acenes **LA2–LA6** are in the range of 188–82 meV and for trans- and cis-acenodithiophenes **S(n)a** and **S(n)b** in the range of 401–89 meV. In the case of acenobisthiophene **S2c–S6c** series, an interesting fact can be observed – the values obtained are ultra small λ_c^+ values (65–29 meV). The smallest hole-reorganization energies reported are those of rigid conjugated macro-cycles like fullerenes, phthalocyanines and discotic molecules in the range of 60–100 meV [5]. Molecules with reorganization energies smaller than 60 meV are rare. For **S4c**, **S5c**, and **S6c** the λ_c^+ values obtained are 36, 33, and 29 meV, respectively.

The B3LYP estimates of λ_a^- values range from 262 to 113 meV for acenes and 375 to 98 meV for positional isomers of acenodithiophenes. Overall, the polaron binding energy for electron transport decreases in the order **S(n)a/b** > **LAa** > **S(n)c**. For example, in the case of molecules having six fused rings the λ_a^- value obtained for **S6a/b** is ca. 134 meV, while for hexacene (**LA6**) it reduces to 113 meV and further to 98 meV for **S6c**. The reorganization energies for electron transport obtained for all molecules are in the range reported for organic systems considered good n-type semiconductors [31–33]. For example, perfluoropentacene has a value of 222 meV while N,N'-dipentyl-3,4,9,10-perylene tetracarboxylicdiimide possesses 272 meV [34,35]. From Table 1, it is clear that the λ_a^- values of **S(n)c** series are slightly lower than those of **LAa** series. The lowest predicted value of 98 meV is of **S6c** and it is a very small value. This indicates that a better electron transport can be achieved with these materials if suitably oriented at the intermolecular level.

To assess the performance of hybrid and meta-hybrid functional we have compared the trends in reorganization energy obtained from B3LYP method with the values predicted by the range separated DFT functional, namely the CAM-B3LYP and wB97XD methods in Figs. 4a and 4b. From the figure it is clear that the reorganization energy values for both hole- and electron-transport calculated with the CAM-B3LYP and wB97XD are larger than the B3LYP estimates. Contrary to B3LYP results here we notice that the cation reorganization energies reach a limiting value for materials having more than four fused rings. Further reduction of cation reorganization energies with increase in number of fused benzene rings is not observed with range separated functionals.

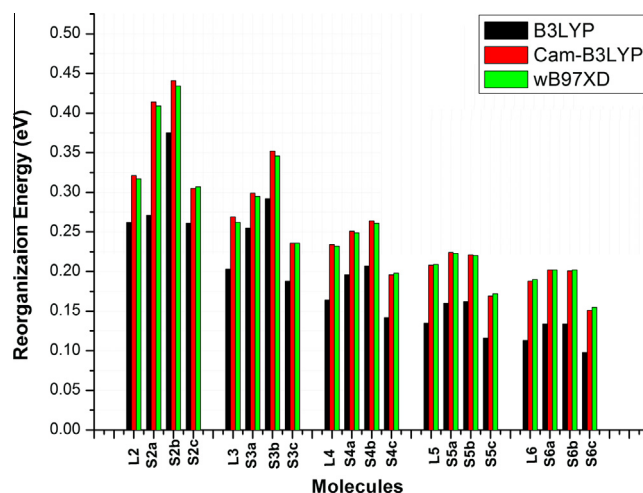


Fig. 4a. Calculated anion reorganization energies obtained using B3LYP, Cam-B3LYP and wB97XD DFT functionals.

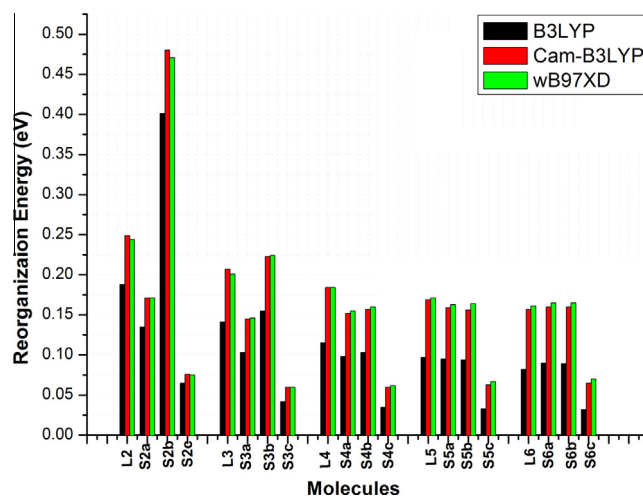


Fig. 4b. Calculated cation reorganization energies obtained using B3LYP, Cam-B3LYP and wB97XD DFT functionals.

The B3LYP values may be slightly underestimated due to delocalization errors whereas the values got from range separated functional may be over estimated due to localization errors that increases the conjugation size. So one has to be very careful in deducting and correlating the results obtained from range separated functionals [36].

Similar to the prediction of B3LYP the λ_a^- values obtained using range separated functionals are larger than the corresponding λ_c^+ values. It is interesting that λ_c^+ values obtained from range separated functionals for **Snc** series is less than 100 meV. All these DFT calculation relatively favors the hole transport easiness than the electron transport for the materials discussed in this work. Also the λ_a^- values got for **S4c**, **S5c** and **S6c** are less than 200 meV. Hence we can expect fairly good electron transport mobility for **S(n)c** series of molecules along with their enhanced hole mobility.

3.2. HOMO, LUMO and HOMO–LUMO gaps

HOMO and LUMO eigen values and HLG are computed at the B3LYP/cc-pVTZ level and are compiled in Table 2. These B3LYP derived frontier orbital energies are compared with the corresponding data obtained with CAM-B3LYP and wB97XD in Figs. 5a and 5b. For all series, the increasing number of fused rings has a destabilizing effect on the HOMO and a stabilizing effect on the LUMO. The HLG is inversely proportional to the acene length.

Even though the DFT analogue of Koopman theorem (*Janak's theorem*) is not derived for a hybrid functional like B3LYP and range separated functionals (CAM-B3LYP and wB97XD), the trends in the calculated vertical ionization energies and electron affinities agree well with the Kohn–Sham orbital energy eigen values [37]. Qualitative results about vertical ionization energies IP and electron affinities EA can be deduced from DFT derived orbital energies ($IP \approx -E_{\text{HOMO}}$ and $EA \approx -E_{\text{LUMO}}$). The IP decreases while the EA increases as the number of intervening rings increases. The **S(n)a** and **S(n)b** series shows relatively good IP values and the IP predicted for **S(n)c** molecules is comparatively lower. But **S(n)c** molecules shows good electron affinity than the linear acenes and other positional isomers **S(n)a** and **S(n)b**. The HLG values obtained for **S(n)c** is very small (Table 2).

The IP (highest occupied energy level of molecular thin films, i.e., experimental HOMO) can be experimentally determined within an accuracy of ± 0.2 eV using ultraviolet photoelectron

spectroscopy [38,39]. The EA (lowest unoccupied energy level of molecular thin films, i.e., experimental LUMO) can also be determined experimentally by using inverse photoelectron spectroscopy (IPES) [39,40]. In the literature we found the experimental HOMO and LUMO values of linear acenes except the hexacene discussed in this work. In Figs. 5a and 5b we compare this experimental data with the DFT predictions. Interestingly one could observe that B3LYP frontier orbital energy values are having a better agreement with the experimental results for both EA and IP. This may be a fortuitous observation but this is common with B3LYP functional for π -systems having biradical character [13,41]. This consensus with experimental data with hybrid GGA's like B3LYP can be ascribed to parameterization in its formalism and self-interaction error (SIE) which mimics the long range pair correlation (non-dynamic correlation) [42]. The over estimation of IP and underestimation of EA by range separated functionals is due to the forceful localization of electrons which may not describe the long range pair correlation in the single determinant formalism even though they are SIE free DFT methods.

3.3. Analysis of molecular orbitals

The energy cost of reorganization can be considered as the activation barrier of an electron/hole transfer. Hence reorganization energy has to be minimized as much as possible to enhance the performance. For the purpose of designing, studying the structural changes upon ionization or capture of an electron can be fruitful. These structural changes are often related to the local bonding character of the frontier molecular orbitals between adjacent atomic sites. The local bonding character can either be bonding, anti-bonding or nonbonding in nature. Upon addition of an electron or a hole to a molecule, one can observe a change in bond order. This can either be a bonding or an anti-bonding interaction between the lobes of the HOMO/LUMO of neighboring atoms. If, for instance, it is a non-bonding interaction, then there is no change in the bond-length. Therefore, one can conclude that the magnitude of reorganization energies reflect the orbital nature of HOMO and LUMO. Hence as a designing principle, the decrease in reorganization energies can be achieved by maximizing the percentage of local nonbonding character in the frontier orbitals between each atomic sites [31,32].

Looking into frontier molecular orbitals thus seemed significant toward our progress. Toward the same aim, we used the B3LYP/6-31G(d,p) level of theory to generate electron density contours of frontier molecular orbitals. We have only provided figures of frontier molecular orbitals of molecules belonging to two ring and six ring systems (Fig. 6). The data for other systems are provided in the supporting information. In general, for the molecules considered here, it was observed that many atomic sites have local non-bonding nature for HOMO and LUMO distribution. For instance, in the case of HOMO of acenes **LA2–LA6** each of the end rings have two bonding and one anti-bonding interaction. At the same time it is observed that there are no electron density lobes at any of the fused carbon sites. In effect, the electron density lobes are seen only at adjacent carbon atoms except at the end rings (non-bonding character). On the contrary in LUMO, as is evident from the figure each of the terminal rings have one bonding and two anti-bonding interactions between adjacent carbon sites. Upon oxidation (creation of hole) or reduction (addition of electron) the structural distortions take place only in the terminal rings. For **S(n)a** and **S(n)b** series, bonding and anti-bonding electron density lobes can even be seen in some fused C–C bonds. Due to this reason, slightly large reorganization energies were obtained for **S(n)a** and **S(n)b** series when compared with those of **LAN** series.

Fascinatingly, all the adjacent atomic sites are having non-bonding nature for the HOMO distribution of **S(n)c** series. Ultra

Table 2
The Kohn–Sham eigen values (HOMO, LUMO) and HLG obtained at B3LYP/cc-pVTZ level of theory.

	HOMO (eV)	LUMO (eV)	HLG (eV)
LA2	–5.79	–0.89	4.90
LA3	–5.23	–1.63	3.59
LA4	–4.86	–2.08	2.78
LA5	–4.60	–2.39	2.21
LA6	–4.41	–2.61	1.80
S2a	–6.03	–0.41	5.62
S3a	–5.49	–0.88	4.61
S4a	–5.10	–1.54	3.55
S5a	–4.80	–2.00	2.80
S6a	–4.58	–2.33	2.25
S2b	–5.85	–0.72	5.13
S3b	–5.47	–1.08	4.39
S4b	–5.09	–1.58	3.51
S5b	–4.80	–2.01	2.79
S6b	–4.58	–2.33	2.25
S2c	–4.77	–1.79	2.98
S3c	–4.38	–2.25	2.13
S4c	–4.17	–2.54	1.63
S5c	–4.03	–2.74	1.29
S6c	–3.94	–2.88	1.06

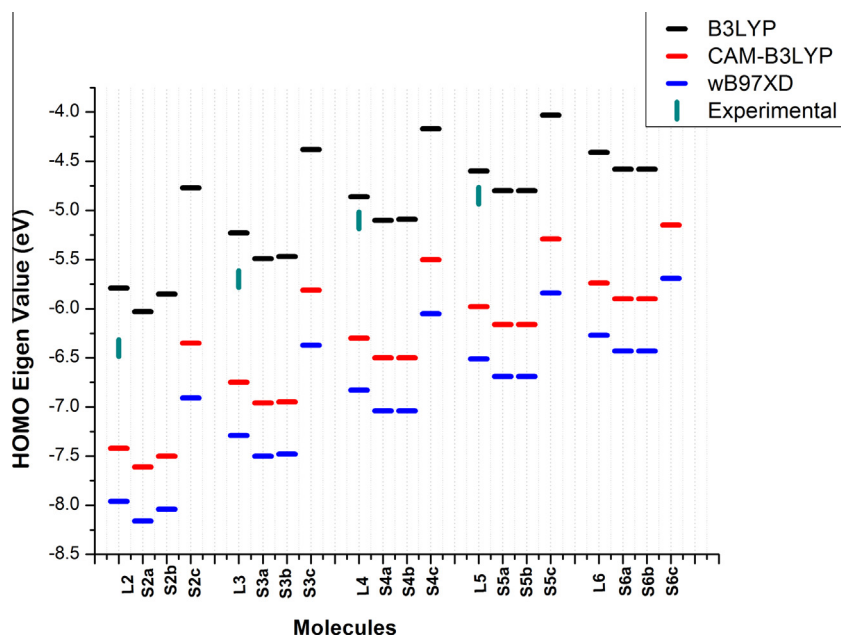


Fig. 5a. HOMO eigenvalue obtained with B3LYP, Cam-B3LYP and wB97XD in this study for all the molecules and compared to the experimental value available for linear acenes.

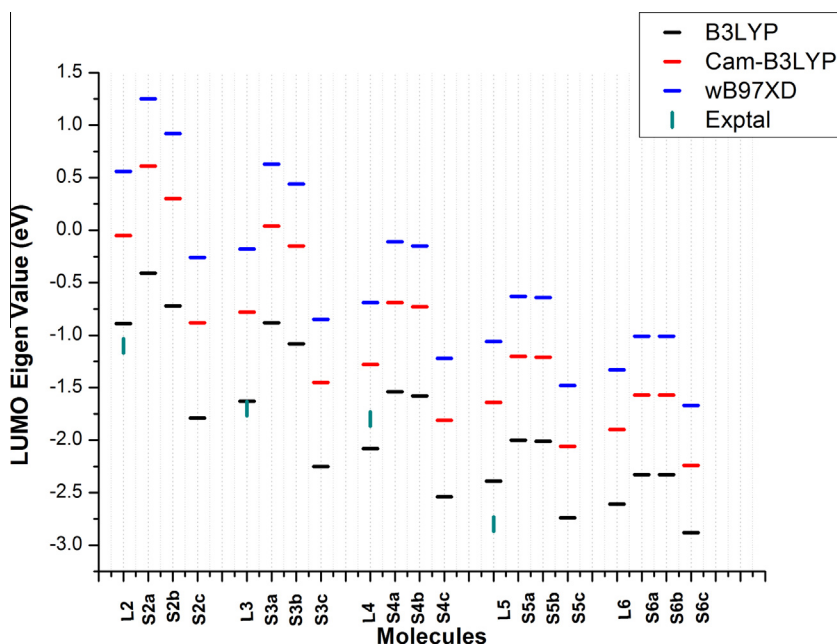


Fig. 5b. LUMO eigenvalue obtained with B3LYP, Cam-B3LYP and wB97XD in this study for all the molecules and compared to the experimental value available for linear acenes.

small λ_c^+ value is the consequence of this complete non-bonding nature. The LUMO distribution clearly brings out the reason for the slightly larger λ_a^- values. The LUMO lobe at the sulfur atom has an anti-bonding interaction with both the adjacent carbon atoms.

3.4. Existence of open-shell nature

The HLG values less than 2.2 eV are obtained for **LA5**, **LA6** and **S3c–S6c**. Such small HLG values and non-bonding nature of frontier molecular orbitals is an indication of the open-shell (biradical) nature of these molecules [43]. The main computational measure

to identify a biradical is the relative value of natural orbital occupation number [44]. From the theoretical point of view, the distinction between biradicals and other ordinary molecules could be better understood based on the natural orbital occupancies of the frontier molecular orbitals. In ordinary molecules, the natural orbital occupancy of HOMO would be two and that of LUMO zero. But in case of biradicals, the HOMO occupancy would be less than two while the LUMO occupancy greater than zero. Depending upon the occupancy value of the LUMO (i.e., 0–1), the biradicaloid character (BRC) can be varying. When the occupancies of HOMO and LUMO becomes exactly one, the frontier molecular orbitals are degenerate, and the molecule can be called a perfect biradical [43,44]. On

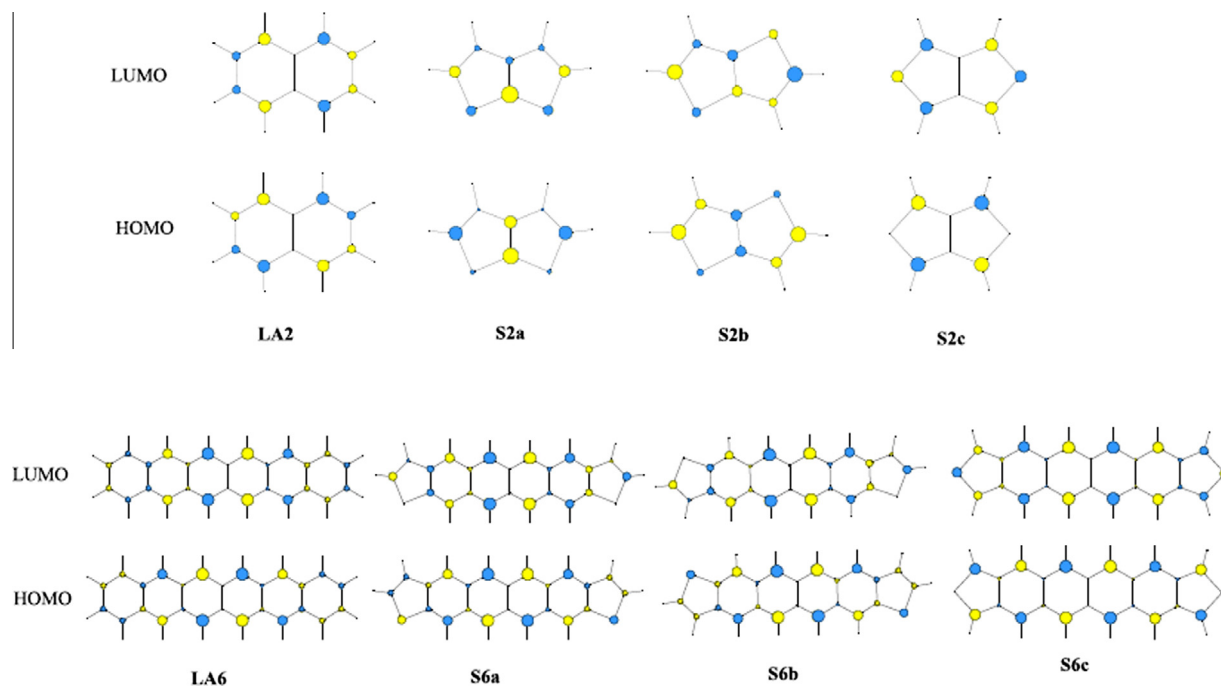


Fig. 6. The spatial distribution of frontier molecular orbitals obtained at B3LYP/6-31G(d) level.

the other hand, if the occupancies of HOMO and LUMO are different, the molecule is a biradicaloid [13,45,46].

While theoretical studies using *ab initio* methods require multi-determinants for their description, accurate post-HF methods such as CASSCF and CCSD are time demanding for large molecules. In this context, defining the biradical in an absolute sense is impractical. Hence relative analysis of natural orbital occupancy is employed to determine whether a molecule is biradical or not. Another simple criterion to determine biradical nature is the singlet–triplet (ST) gap and is usually small for biradicaloids [43]. The ST gap can be computationally estimated accurately using multi-reference methods like CASSCF/CASPT2 or spin-flip EOM-CCSD [47]. For relatively large systems, we can use spin-unrestricted DFT or SF-TDDFT methods [47]. One advantage of the SF-TDDFT/TDA method is that the distinction between biradicals and other ordinary molecules can be better understood, as this method is known to take care of the multi-reference nature from a computationally cheap single reference formalism. The SF method as implemented in Qchem was based on a collinear kernel and hence authors suggested to use hybrid DFT method with a large fraction of Hartree–Fock (HF) exchange. Here, the SF calculations have been carried out with the 50–50 functional (50% HF exchange) combined with moderate 6-31G(d) basis set. The char-

acter of ground state electronic configurations and their leading SF amplitude for the studied molecules are given in Table 3. From the table it is clear that the lower acenes **LA2–4**, **S(n)a**, and **S(n)b** series have a closed shell configuration, whereas, the pentacene, hexacene, and **S(n)c** molecules exhibit an open-shell nature. The SF-TDDFT method predicts a singlet ground state for all the molecules.

The study clearly revealed that maximizing the percentage of nonbonding nature in frontier molecular orbitals is a key factor to reduce the reorganization energies as suggested by Chang et al. [31,32]. Also it is well known that biradical molecules have singly occupied degenerate non-bonding orbitals [46]. Therefore one can envisage that lifting the orbital degeneracy of a biradical by a suitable geometric perturbation leads to a stable biradicaloid molecule. Interestingly such biradicaloid molecules retain the non-bonding orbital nature from the parent biradical. This preservation of the non-bonding character in HOMO and LUMO leads to small reorganization energy. With this motivation we looked into the literature to see if any experimentally reported stable biradicaloid molecules show enhanced conductance. Koike et al. have shown high ambipolar mobilities for diphenyl derivative of *s*-indacenodiphenalene biradicaloids [48]. Another experimentally reported ambipolar material polymer of benzobisthiadiazole also

Table 3

The spin value and leading amplitudes of electronic configuration of ground state for the molecules under study obtained from SF-TDDFT/TDA method using 50–50 functional and 6-31G(d) basis set.

Mol.	$\langle S^2 \rangle$	Amplitude	Mol.	$\langle S^2 \rangle$	Amplitude	Mol.	$\langle S^2 \rangle$	Amplitude	Mol.	$\langle S^2 \rangle$	Amplitude
LA2	0.09	$S(2) \rightarrow S(1) = 0.99\alpha$	S2a	0.04	$S(2) \rightarrow S(1) = 0.99\alpha$	S2b	0.14	$S(2) \rightarrow S(1) = 0.99\alpha$	S2c	0.11	$S(2) \rightarrow S(1) = 0.97\alpha$
LA3	0.09	$S(2) \rightarrow S(1) = 0.98\alpha$	S3a	0.09	$S(2) \rightarrow S(1) = 0.99\alpha$	S3b	0.15	$S(2) \rightarrow S(1) = 0.99\alpha$	S3c	0.15	$S(2) \rightarrow S(1) = 0.95\alpha$
LA4	0.12	$S(2) \rightarrow S(1) = 0.98\alpha$	S4a	0.11	$S(2) \rightarrow S(1) = 0.98\alpha$	S4b	0.13	$S(2) \rightarrow S(1) = 0.99\alpha$	S4c	0.19	$S(2) \rightarrow S(1) = 0.93\alpha$
LA5	0.14	$S(2) \rightarrow S(1) = 0.97\alpha$ $S(1) \rightarrow S(2) = -0.16\alpha$	S5a		$S(2) \rightarrow S(1) = 0.98\alpha$	S5b	0.12	$S(2) \rightarrow S(1) = 0.98\alpha$	S5c	0.24	$S(2) \rightarrow S(1) = 0.90\alpha$
LA6	0.16	$S(2) \rightarrow S(1) = 0.96\alpha$ $S(1) \rightarrow S(2) = -0.20\alpha$	S6a	0.14	$S(2) \rightarrow S(1) = 0.97\alpha$	S6b	0.14	$S(2) \rightarrow S(1) = 0.97\alpha$	S6c	0.28	$S(2) \rightarrow S(1) = 0.86\alpha$ $S(1) \rightarrow S(2) = -0.41\alpha$

has biradicaloid nature [49]. So we suggest that the biradicaloid approach is another design guideline to explore organic materials with enhanced charge carrier transport properties.

A major impediment toward the synthesis of these molecules is their stability. But it is possible to stabilize such molecules either by a suitable geometric modification for effective spin delocalization [50] or by creating large zwitterionic contributions to the ground state structure [51]. Further, air stability can be achieved by lowering the LUMO level below the reduction potentials of Oxygen. This can be realized by substituting the C–H group by Nitrogen atoms [8].

4. Conclusion

The electronic structure of positional isomers of dithienoacene (**S2a–c**) benzodithiophene (**S3a–c**), naphthodithiophene (**S4a–c**), anthradithiophene (**S5a–c**), and tetracenodithiophene (**S6a–c**) have been studied at B3LYP/cc-pVTZ level and compared with structural analogues of oligoacenes from naphthalene to hexacene (**LA2–6**). The reorganization energies associated with the intermolecular transport of an electron/hole, and frontier molecular orbitals along with energy levels were considered to determine the charge carrier mobilities of these molecules. Extremely small reorganization energy values are obtained for **S(n)c** series which has a non-bonding molecular orbital in the HOMO and LUMO. This study strongly suggests that the **S(n)c** series are promising materials with high ambipolar mobility. It is also shown that biradicaloid molecules have small reorganization energies for hole and electron transport due to the preservation of nearly non-bonding nature in the HOMO and LUMO.

Acknowledgements

The author A.T. thanks the Chairman (Honorable Minister of Transport, Kerala) and the Principal, Dr. Jayasudha J.S. of SreeChitraThirunal Engineering College, Trivandrum for their constant encouragement towards the project. One of the authors J.J. acknowledges the support by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (No. NRF-2012M3C1A6035363).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.comptc.2016.05.001>.

References

- [1] M. Mas-Torrent, C. Rovira, Novel small molecules for organic field-effect transistors: towards processability and high performance, *Chem. Soc. Rev.* 37 (2008) 827–838, <http://dx.doi.org/10.1039/b614393h>.
- [2] H. Klauk, Organic thin-film transistors, *Chem. Soc. Rev.* 39 (2010) 2643–2666, <http://dx.doi.org/10.1039/b909902f>.
- [3] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, Dye-sensitized solar cells, *Chem. Rev.* 110 (2010) 6595–6663, <http://dx.doi.org/10.1002/chem.201101923>.
- [4] A.W. Hains, Z. Liang, M.A. Woodhouse, B.A. Gregg, Molecular semiconductors in organic photovoltaic cells, *Chem. Rev.* 110 (2010) 6689–6735, <http://dx.doi.org/10.1021/cr9002984>.
- [5] V. Coropceanu, J. Cornil, D.A. da Silva Filho, Y. Olivier, R. Silbey, J.-L. Bredas, Charge transport in organic semiconductors, *Chem. Rev.* 107 (2007) 926–952, <http://dx.doi.org/10.1021/cr050140x>.
- [6] M.A. Reddy, A. Thomas, K. Srinivas, V.J. Rao, K. Bhanuprakash, B. Sridhar, et al., Synthesis and characterization of 9,10-bis(2-phenyl-1,3,4-oxadiazole) derivatives of anthracene: efficient n-type emitter for organic light-emitting diodes, *J. Mater. Chem.* 19 (2009) 6172–6184, <http://dx.doi.org/10.1039/b905808g>.
- [7] A.L. Appleton, S.M. Brombosz, S. Barlow, J.S. Sears, J.-L. Bredas, S.R. Marder, et al., Effects of electronegative substitution on the optical and electronic

- properties of acenes and diazaacenes, *Nat. Commun.* 1 (2010) 91, <http://dx.doi.org/10.1038/ncomms1088>.
- [8] A.N. Sokolov, S. Atahan-Evrenk, R. Mondal, H.B. Akkerman, R.S. Sánchez-Carrera, S. Granados-Focil, et al., From computational discovery to experimental characterization of a high hole mobility organic crystal, *Nat. Commun.* 2 (2011) 437, <http://dx.doi.org/10.1038/ncomms1451>.
- [9] R. Mondal, S. Ko, Z. Bao, Fused aromatic thienopyrazines: structure, properties and function, *J. Mater. Chem.* 20 (2010) 10568–10576, <http://dx.doi.org/10.1039/C0JM01840F>.
- [10] G. Qian, Z.Y. Wang, Near-infrared organic compounds and emerging applications, *Chem. – Asian J.* 5 (2010) 1006–1029, <http://dx.doi.org/10.1002/asia.200900596>.
- [11] C. Wang, H. Dong, W. Hu, Y. Liu, D. Zhu, Semiconducting π -conjugated systems in field-effect transistors: a material odyssey of organic electronics, *Chem. Rev.* 112 (2012) 2208–2267, <http://dx.doi.org/10.1021/cr100380z>.
- [12] A.P. Kulkarni, C.J. Tonzola, A. Babel, S.A. Jenekhe, Electron transport materials for organic light-emitting diodes, *Chem. Mater.* 16 (2004) 4556–4573, <http://dx.doi.org/10.1021/cm049473l>.
- [13] A. Thomas, K. Bhanuprakash, Comparative study of the semiconducting properties of benzothiadiazole and benzobis(thiadiazole) derivatives using computational techniques, *ChemPhysChem* 13 (2012) 597–605, <http://dx.doi.org/10.1002/cphc.201100565>.
- [14] N.L. Janaki, B. Priyanka, A. Thomas, K. Bhanuprakash, A computational study of semiconducting benzobisthiazoles: analysis of the substituent effects on the electronic structure, solid-state interactions, and charge transport properties using DFT methods, *J. Phys. Chem. C* 116 (2012) 22663–22674, <http://dx.doi.org/10.1021/jp304892x>.
- [15] J.L. Brédas, D. Beljonne, V. Coropceanu, J. Cornil, Charge-transfer and energy-transfer processes in π -conjugated oligomers and polymers: a molecular picture, *Chem. Rev.* 104 (2004) 4971–5003, <http://dx.doi.org/10.1021/cr040084k>.
- [16] J.C. Sancho-García, A.J. Pérez-Jiménez, Y. Olivier, J. Cornil, Molecular packing and charge transport parameters in crystalline organic semiconductors from first-principles calculations, *Phys. Chem. Chem. Phys.* 12 (2010) 9381–9388, <http://dx.doi.org/10.1039/B925652K>.
- [17] S. Mi, N. Lu, Impact of substitution on the reorganization energy of bis-triarylamine derivatives, *J. Mol. Struct. THEOCHEM.* 940 (2010) 1–5, <http://dx.doi.org/10.1016/j.theochem.2009.09.053>.
- [18] R. Zhu, Y.-A. Duan, Y. Geng, C.-Y. Wei, X.-Y. Chen, Y. Liao, Theoretical evaluation on the reorganization energy of five-ring-fused benzothiophene derivatives, *Comput. Theor. Chem.* 1078 (2016) 16–22, <http://dx.doi.org/10.1016/j.comptc.2015.12.017>.
- [19] R.A. Marcus, On the theory of oxidation–reduction reactions involving electron transfer. I, *J. Chem. Phys.* 24 (1956) 966, <http://dx.doi.org/10.1063/1.1742723>.
- [20] S.E. Koh, C. Risko, D.A. Da Silva Filho, O. Kwon, A. Facchetti, J.L. Brédas, et al., Modeling electron and hole transport in fluoroarene-oligothiophene semiconductors: investigation of geometric and electronic structure properties, *Adv. Funct. Mater.* 18 (2008) 332–340, <http://dx.doi.org/10.1002/adfm.200700713>.
- [21] G. Zhang, C.B. Musgrave, Comparison of DFT methods for molecular orbital eigenvalue calculations, *J. Phys. Chem. A* 111 (2007) 1554–1561, <http://dx.doi.org/10.1021/jp061633o>.
- [22] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, et al., Gaussian 09, Revision A.02, vol. 34, Gaussian Inc., Wallingford, CT, 2009, <http://dx.doi.org/10.1159/000348293>.
- [23] A.D. Becke, Density-functional thermochemistry. III. The role of exact exchange, *J. Chem. Phys.* 98 (1993).
- [24] T. Yanai, D.P. Tew, N.C. Handy, A new hybrid exchange–correlation functional using the Coulomb-attenuating method (CAM-B3LYP), *Chem. Phys. Lett.* 393 (2004) 51–57, <http://dx.doi.org/10.1016/j.cplett.2004.06.011>.
- [25] J.-D. Chai, M. Head-Gordon, Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections, *Phys. Chem. Chem. Phys.* 10 (2008) 6615–6620, <http://dx.doi.org/10.1039/B810189B>.
- [26] U. Salzner, A. Aydin, Improved prediction of properties of π -conjugated oligomers with range-separated hybrid density functionals, *J. Chem. Theory Comput.* 7 (2011) 2568–2583, <http://dx.doi.org/10.1021/ct2003447>.
- [27] D. Fazzi, M. Caironi, C. Castiglioni, Quantum-chemical insights into the prediction of charge transport parameters for a naphthalenetetracarboxydiimide-based copolymer with enhanced electron mobility, *J. Am. Chem. Soc.* 133 (2011) 19056–19059, <http://dx.doi.org/10.1021/ja208824d>.
- [28] Y. Shao, L.F. Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S.T. Brown, et al., Advances in methods and algorithms in a modern quantum chemistry program package, *Phys. Chem. Chem. Phys.* 8 (2006) 3172–3191, <http://dx.doi.org/10.1039/B517914A> (QChem 3.1, Q-Chem Inc, Pittsburgh, PA, 2007).
- [29] Y.A. Bernard, Y. Shao, A.I. Krylov, General formulation of spin-flip time-dependent density functional theory using non-collinear kernels: theory, implementation, and benchmarks, *J. Chem. Phys.* 136 (2012), <http://dx.doi.org/10.1063/1.4714499>.
- [30] O. Kwon, V. Coropceanu, N.E. Gruhn, J.C. Durivage, J.G. Laquindanum, H.E. Katz, et al., Characterization of the molecular parameters determining charge transport in anthradithiophene, *J. Chem. Phys.* 120 (2004).
- [31] Y.-C. Chang, I. Chao, An important key to design molecules with small internal reorganization energy: strong nonbonding character in frontier orbitals, *J. Phys. Chem. Lett.* 1 (2010) 116–121, <http://dx.doi.org/10.1021/jz900042x>.

- [32] H.-Y. Chen, I. Chao, Effect of perfluorination on the charge-transport properties of organic semiconductors: density functional theory study of perfluorinated pentacene and sexithiophene, *Chem. Phys. Lett.* 401 (2005) 539–545, <http://dx.doi.org/10.1016/j.cplett.2004.11.125>.
- [33] M.-Y. Kuo, C.-C. Liu, Molecular design toward high hole mobility organic semiconductors: tetraceno[2,3-c]thiophene derivatives of ultrasmall reorganization energies, *J. Phys. Chem. C* 113 (2009) 16303–16306, <http://dx.doi.org/10.1021/jp9065423>.
- [34] M.C.R. Delgado, E.-G. Kim, D.A. da Silva Filho, J.-L. Bredas, Tuning the charge-transport parameters of perylene diimide single crystals via end and/or core functionalization: a density functional theory investigation, *J. Am. Chem. Soc.* 132 (2010) 3375–3387, <http://dx.doi.org/10.1021/ja908173x>.
- [35] R.J. Chesterfield, J.C. McKeen, C.R. Newman, P.C. Ewbank, D.A. Da Silva Filho, J.L. Brédas, et al., Organic thin film transistors based on N-alkyl perylene diimides: charge transport kinetics as a function of gate voltage and temperature, *J. Phys. Chem. B* 108 (2004) 19281–19292, <http://dx.doi.org/10.1021/jp046246y>.
- [36] T. Körzdörfer, R.M. Parrish, J.S. Sears, C.D. Sherrill, J.-L. Brédas, On the relationship between bond-length alternation and many-electron self-interaction error, *J. Chem. Phys.* 137 (2012), <http://dx.doi.org/10.1063/1.4752431>.
- [37] M. Winkler, K.N. Houk, N-rich oligoacene n-channel organic semiconductor, *J. Am. Chem. Soc.* 129 (2007) 1805–1815. <http://pubs3.acs.org/acs/journals/doi/lookup?in_doi=10.1021/ja067087u>.
- [38] S.M. Tadayyon, H.M. Grandin, K. Griffiths, L.L. Coatsworth, P.R. Norton, H. Aziz, et al., Reliable and reproducible determination of work function and ionization potentials of layers and surfaces relevant to organic light emitting diodes, *Org. Electron.* 5 (2004) 199–205, <http://dx.doi.org/10.1016/j.orgel.2003.12.002>.
- [39] P.I. Djurovich, E.I. Mayo, S.R. Forrest, M.E. Thompson, Measurement of the lowest unoccupied molecular orbital energies of molecular organic semiconductors, *Org. Electron.* 10 (2009) 515–520, <http://dx.doi.org/10.1016/j.orgel.2008>.
- [40] D. Cahen, A. Kahn, Electron energetics at surfaces and interfaces: concepts and experiments, *Adv. Mater.* 15 (2003) 271–277, <http://dx.doi.org/10.1002/adma.200390065>.
- [41] A. Thomas, K. Srinivas, C. Prabhakar, K. Bhanuprakash, V.J. Rao, Estimation of the first excitation energy in diradicaloid croconate dyes having absorption in the near infra red (NIR): a DFT and SF-TDDFT study, *Chem. Phys. Lett.* 454 (2008) 36–41, <http://dx.doi.org/10.1016/j.cplett.2008.01.074>.
- [42] D. Cremer, M. Filatov, V. Polo, E. Kraka, S. Shaik, Implicit and explicit coverage of multi-reference effects by density functional theory, *Int. J. Mol. Sci.* 3 (2002) 604, <http://dx.doi.org/10.3390/i3060604>.
- [43] J. Fabian, R. Zahradnik, The search for highly colored organic compounds, *Angew. Chem. Int. Ed. Engl.* 28 (1989) 677–694, <http://dx.doi.org/10.1002/anie.198906773>.
- [44] M. Nakano, T. Nitta, K. Yamaguchi, B. Champagne, E. Botek, Spin multiplicity effects on the second hyperpolarizability of an open-shell neutral π -conjugated system, *J. Phys. Chem. A* 108 (2004) 4105–4111, <http://dx.doi.org/10.1021/jp0496371>.
- [45] A. Thomas, K. Bhanuprakash, K.M.M.K. Prasad, Near infrared absorbing benzobis(thiadiazole) derivatives: computational studies point to biradical nature of the ground states, *J. Phys. Org. Chem.* 24 (2011) 821–832.
- [46] A. Thomas, Theoretical Studies of Structure and Properties of Biradicaloid Molecules, Andhra University, 2011. November, <http://eprints.csirexplorations.com/937/1/Abstract_Anup.pdf>.
- [47] Y. Shao, M. Head-Gordon, A.I. Krylov, The spin-flip approach within time-dependent density functional theory: theory and applications to diradicals, *J. Chem. Phys.* 118 (2003) 4807–4818, <http://dx.doi.org/10.1063/1.1545679>.
- [48] H. Koike, M. Chikamatsu, R. Azumi, J. Tsutsumi, K. Ogawa, W. Yamane, et al., Stable delocalized singlet biradical hydrocarbon for organic field-effect transistors, *Adv. Funct. Mater.* (2015), <http://dx.doi.org/10.1002/adfm.201503650>.
- [49] J.D. Yuen, M. Wang, J. Fan, D. Sheberla, M. Kemei, N. Banerji, et al., Importance of unpaired electrons in organic electronics, *J. Polym. Sci., Part A: Polym. Chem.* 53 (2015) 287–293, <http://dx.doi.org/10.1002/pola.27321>.
- [50] A. Shimizu, M. Nakano, Y. Hirao, T. Kubo, Experimental consideration of covalent-bonding interactions in stacks of singlet biradicals having Kekulé structures, *J. Phys. Org. Chem.* 24 (2011) 876–882, <http://dx.doi.org/10.1002/poc.1873>.
- [51] A. Thomas, G. Krishna Chaitanya, K. Bhanuprakash, K.M.M. Krishna Prasad, Substituents destabilize the molecule by increasing biradicaloid character and stabilize by intramolecular charge transfer in the derivatives of benzobis(thiadiazole) and thiadiazolothienopyrazine: a computational study, *ChemPhysChem* 12 (2011) 3458–3466, <http://dx.doi.org/10.1002/cphc.201100701>.