

Theoretical modelling of low band-gap organic oligomers

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Abstract

Two low band-gap polymers (gap energy ~ 1 eV) based on carbon-bridged dithienyl monomers have been investigated by density functional theory (B3LYP/6-31G) and semiempirical/CI methods. Theoretical absorption spectra from monomers to pentamers were obtained and showed good agreement with the experimental spectra of the polymers. Comparison with data for oligomers of CDM and BDT (dithiophene derivatives) indicated that the new polymers have a small band gap and could fulfill the conditions for n-dopability.

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1. Introduction

Semiconducting polymers with band-gaps in the range 0.5–3.0 eV have a number of potential advantages over their inorganic counterparts, such as ease of processing, cost of manufacture and greater variety. These classes of conjugated polymers are studied since the first work on electroluminescence properties [1–4]. In fact, these polymers have interesting physical properties but also the emission can be modified by chemical methods to yield various light colors by red or blue shift of the emission band [5]. These emissions could be obtained by adding substituted chains with drawing electron properties such as alkoxy or by introducing non-conjugated units in the backbone of the polymer. These polymers have interesting properties, for example the light emission can be modified by using chemical methods to yield various light colors from red or blue shift of the emission band [5] by adding substituted chains with drawing electron properties such as alkoxy or by introducing non-conjugated units in the backbone of the polymer. Thus, a lot of research groups have investigated

the optimization of the conversion process towards using the material in high quality devices [6–11].

To decrease the bandgap (E_G) of a polymer system, the monomer structure must be tailored in such a way as to increase the quinoid character of the extended π -conjugated system, thus decreasing its aromaticity [12].

One suitable method of achieving this involves the introduction of electron-withdrawing groups at the sp^2 carbon bridging the bridging on 4, 4'-positions of a bithienyl precursor. Ferraris and Lambert [13,14] produced, by electropolymerisation, the polymer poly(4-dicyano methylene-4H-cyclopenta[2,1-:3,4b']dithiophene) (PCDM) and 1,3-benzodithiole-4H-cyclopenta[2,1-b:3,4-b']dithiophene (BDT) [15] with band-gap of the resulting film was reported to be less film less than 1 eV [14].

In this work we presented the results of a theoretical study of electronic transitions in oligomers of CDM and BDT.

2. Methodology

The size of the molecules CDM [BDT] have 20 [34], 38 [66], 56 [98], 74 [130] and 92 [162] atoms for 1, 2, 3, 4 and 5 oligomeric units presented in this work.

In this work we performed calculations from the monomer to the pentamer oligomeric units for both CDM and BDT systems. Therefore the number of atoms considered on each

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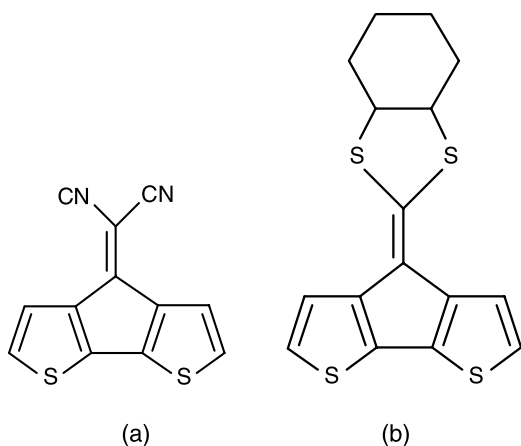


Fig. 1. The structures of (a) CDM and (b) BDT monomers.

oligomer is given by $18n + 2$ (CDM) and $32n + 2$ (BDT) where n is the number of monomer units. The molecules chemical structures are shown in Fig. 1.

Semiempirical approaches such as the ones contained in MOPAC package [16], employed as well density functional theory (B3LYP (Becke's three-parameter hybrid method [17] with Lee, Yang and Parr correlation [18])). The standard 6-31G basis sets were used for all B3LYP calculations. The geometries have been carried out using B3LYP [17,18], PM3 [19] and AM1 [19] level. For MOPAC package we utilized a RMS gradient equal to $0.05 \text{ kcal mol}^{-1} \text{ \AA}^{-1}$. The criteria for terminating all optimizations, electronic and geometric, were increased by a factor of 100. We believe these options yield the best overall results [20]. The convergence criteria for the energy calculations and geometry optimizations used in the density functional methods were default parameters in the Gaussian program [21].

As is usual with methods without the electronic correlation, the optical transitions are substantially overestimated. Owing to this we have used the INDO methods. Absorption spectra calculations were made using the ZINDO package [22] with geometry being fully optimised by B3LYP/6-31G. All calculations were made at the INDO/S-CI (Intermediate Neglect of Differential Overlap/Spectroscopy—Configuration Interaction) level. This method was parameterised to give the best description of the UV–visible optical transitions, particularly for organic materials [20]. Each one of such calculations typically used up to 280 (singlet) configurations [23].

3. Structures

The most probable geometrical structures for the dimer of each molecule were found to be essentially planar, and with the configurations denoted by (a) or (b) in Fig. 2 which were optimised using semiempirical calculations at the PM3 and AM1 levels.

We adopted for molecule (a) the notation ud and for molecule (b) the notation dd (please note that dd is equal to parallel and ud antiparallel configuration and $du = ud$; $dd = uu$ (d came from down and u came from up)).

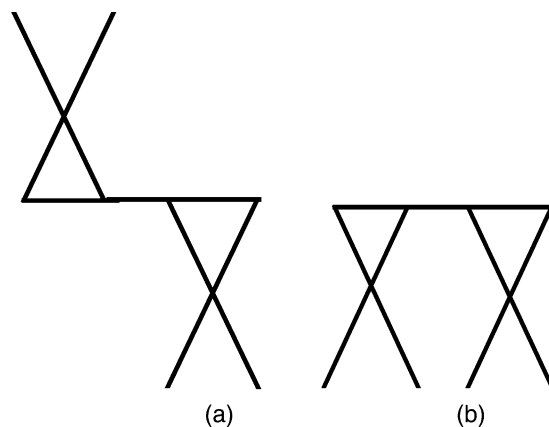


Fig. 2. Diagram depicting (a) a hypothetical parallel dimer configuration and (b) a hypothetical antiparallel dimer configuration utilized in this work.

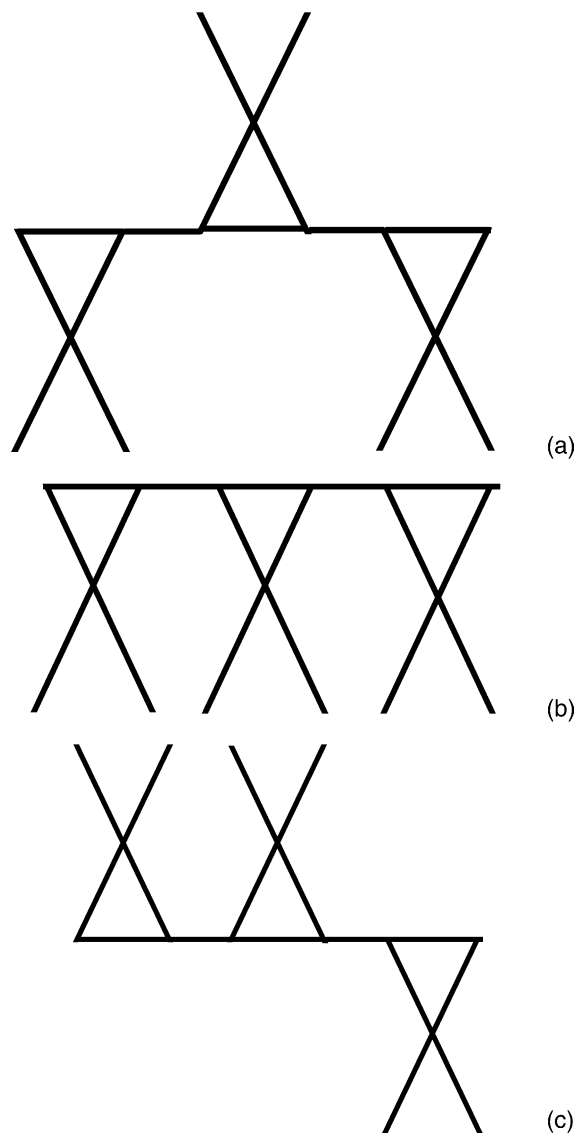


Fig. 3. Diagram depicting a hypothetical (a) antiparallel 1, (b) parallel and (c) antiparallel 2 trimer configuration.

Table 1

Dipole moment, electronic energies and heat of formation, for geometries calculated by B3LYP/6-31G, PM3 and AM1 of CDM and BDT in the ground state

Molecular geometry	Dipole moment (Debye)	Heat of formation, ΔF (Kcal/mol)	Dipole moment (Debye)	Heat of formation, ΔF (Kcal/mol)	Dipole moment (Debye)	Electronic energy (Kcal/mol)
	PM3		AM1		DFT/6-31G	
CDM (m)	3.7	174.9	6.3	164.1	4.27	-856727.05
CDM (d) ^a	0.0	356.1	0.0	329.8	0.00	-1712709.39
CDM (d) ^b	6.7	356.0	11.7	332.0	7.75	-1712707.55
CDM (tr) ^a	3.6	537.4	6.2	495.7	4.06	-2568691.95
CDM (tr) ^b	9.8	537.2	16.0	500.0	10.99	-2568688.42
CDM (tr) ^c	3.3	537.2	5.9	498.6	3.69	-2568690.11
CDM (tet) ^a	0.0	718.7	0.0	661.6	0.04	-3424674.20
CDM (tet) ^b	12.5	718.4	18.6	664.1	14.95	-3424673.28
CDM (tet) ^c	6.4	718.4	16.2	665.6	7.26	-3424670.83
CDM (tet) ^d	0.3	718.2	0.8	663.4	0.33	-3424672.67
CDM (pent) ^a	3.6	899.7	6.1	827.4	4.03	-4280656.76
CDM (pent) ^b	14.9	899.2	24.4	836.7	17.51	-4280655.23
CDM (pent) ^c	3.4	899.6	5.3	829.3	3.98	-4280655.60
CDM (pent) ^d	9.7	899.4	15.9	831.3	11.97	-4280655.31
CDM (pent) ^e	3.2	899.5	5.2	829.4	3.95	-4280655.70
CDM (pent) ^f	2.9	899.2	4.7	831.1	3.96	-4280655.27
BDT (m)	4.1	104.5	2.1	85.8	6.81	-1387184.05
BDT (d) ^a	0.0	212.5	0.0	173.4	0.11	-2773636.09
BDT (d) ^b	7.9	212.1	3.9	173.8	13.01	-2773634.25
BDT (tr) ^a	4.0	324.5	2.1	262.6	6.74	-4160076.64
BDT (tr) ^b	11.6	323.6	6.6	264.4	17.94	-4160073.27
BDT (tr) ^c	3.9	324.0	2.3	263.6	6.07	-4160075.11
BDT (tet) ^a	0.0	432.9	0.0	349.6	1.80	-5546523.93
BDT (tet) ^b	14.9	431.5	8.7	352.4	21.95	-5546518.41
BDT (tet) ^c	7.7	431.9	4.7	351.4	12.68	-5546521.48
BDT (tet) ^d	0.3	432.4	0.4	350.5	0.30	-5546522.09
BDT (pent) ^a	3.9	541.7	2.1	438.7	6.72	-6932964.48
BDT (pent) ^b	17.8	539.8	10.5	440.5	28.60	-6932963.25
BDT (pent) ^c	3.9	544.2	2.4	439.4	6.70	-6932965.02
BDT (pent) ^d	11.3	543.7	6.8	440.2	19.98	-6932963.87
BDT (pent) ^e	3.9	543.1	2.4	439.6	6.67	-6932964.04
BDT (pent) ^f	3.8	543.7	2.7	440.5	6.65	-6932964.35

m, d, tr, tet and pent denotes monomer, dimer, trimer, tetramer and pentamer respectively; Note that the possible geometrical structures for the conformers are commented in Section 3. The pentamer calculated in this work are the parallel and anti-parallel conformers. The error bars of semiempirical methods for the heat of formation are equal to ± 2 kcal/mol.

In the same way, for trimer molecules we have three possible configurations showed in Fig. 3. Utilizing the same kind of notation we adopted for molecule (a) antiparallel 1 (*dud*), (b) parallel (*ddd*) and (c) antiparallel 2 (*uud*).

The tetramer structure has five possibilities and there are: (a) *dudu*, (b) *dddd*, (c) *duuu* and (d) *duud*. We considered six possibilities for pentamer structure: (a) *dudud*, (b) *dddd*, (c) *ddudu*, (d) *uuduu*, (e) *duudu*, (f) *duuud*.

4. Results and discussion

The experimental UV–visible absorption spectra for both polymers shows a broad, long wavelength absorption feature consistent with π – π^* transition centered at 950 nm [14] (PCDM) and 626 nm [24] (PBDT).

Table 1 shows the dipole moments and heats of formation for the monomer (m), dimer (d), trimer (tr), tetramer (tet) and pentamer (pent) of CDM and BDT, calculated using semiempirical and DFT techniques. The geometrical structures for each molecule were found to be planar and the configurations are schematically shown in Figs. 2 and 3.

The dipole moments for the parallel arrangements from dimer to pentamer are almost equal to an integer multiple of the monomer dipole moment, as would be expected from a simple summation of non-interacting monomer moments. This is not an

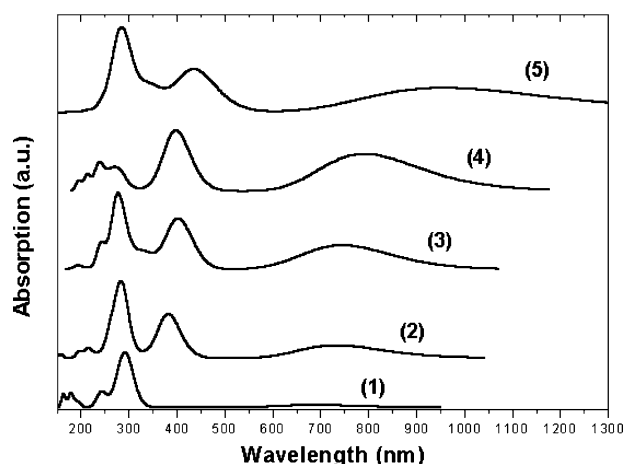


Fig. 4. Theoretical UV–visible ground-state absorption spectra for (1) monomer, (2) dimer, (3) trimer, (4) tetramer and (5) pentamer of CDM.

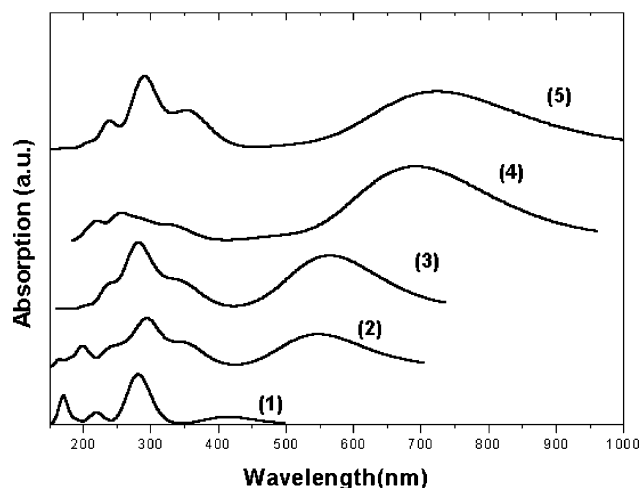


Fig. 5. Theoretical UV-visible ground-state absorption spectra for (1) monomer, (2) dimer, (3) trimer, (4) tetramer and (5) pentamer of BDT.

artificial results as point out in reference [25]. In these cited work semiempirical, ab initio and density functional calculations of small oligomers of carbonitrile were performed. The goal was to investigate the *cis/trans* molecular stability. All employed methodologies presented the same qualitative results.

When one of the monomers adopts an antiparallel configuration the calculation shows a significant reduction of the dipole moment from the odd to the even oligomer. So that as far the dipole moment remains significantly above zero indicates strong intermonomer interactions if we have the later configuration.

It is important note that the ground state energies and the heats of formation for the isomers of the respective materials are quite similar. This is an indication of equal probabilities for the existence of the various configurations considered.

In the Figs. 4 and 5 one may compare the theoretical absorptions spectra for CDM and BDT systems. These spectral curves were obtained from normalized gaussian functions weighted by the oscillator strengths. Full details of the calculations can be found elsewhere [23].

For CDM monomer one can see a smooth band at ≈ 700 nm which has an oscillator strength (o.s.) of 0.10. This band corresponds essentially to a pure $|H \rightarrow L\rangle$ transition, i.e. a transition from the highest occupied (H) to the lowest unoccupied (L) molecular orbital, while the band at ≈ 300 nm corresponds to a mixing of the transitions $|H-2 \rightarrow L+1\rangle$ and $|H-3 \rightarrow L+2\rangle$ (with equal coefficients of 0.5) with o.s. = 0.91. For CDM dimer the band at ≈ 750 nm has an oscillator strength (o.s.) of 0.16 and it is a pure $|H \rightarrow L\rangle$ transition,

resulting an increasing of its importance when compared with monomer result. The most important bands occur between 250 and 400 nm and corresponds to a mixing of different transitions, $|H \rightarrow L\rangle$, $|H-1 \rightarrow L+1\rangle$, $|H-3 \rightarrow L\rangle$ and $|H-2 \rightarrow L\rangle$. Finally, the theoretical spectra of the trimers and tetramers are seen to be red-shifted compared with their respective monomers and dimers (Fig. 4), a trend, which continues with the increasing of the oligomer chain length. These behaviors are followed for pentamers in the main band and it is possible to see a very pronounced peak at low energy, compared with others oligomers. The reason for that is the inclusion of a mixing of different transitions. The same behavior are observed for BDT molecules (Fig. 5).

These trend is also clearly seen in Table 2 which shows the energies of the $\pi-\pi^*$ transitions (corresponding to the long wavelength transitions) in the monomer, dimer, trimer, tetramer, pentamer and polymer systems. The data also confirms that by bridging two thiophene moieties with electron-withdrawing groups a significant reduction in the bandgap of the resulting polymer may be achieved if compared with polymers based on the 3-alkylthiophenes (LUMO-HOMO = 1.67 eV [26]).

Finally, we would like to emphasize here that the band-gaps results, as collected on Table 2, for the pentamers are almost the same as for the polymer (experimental). Therefore it could be taken as a proof that the calculations on the pentamers are good enough to be considered as a fair representation to study of the polymers properties.

5. Conclusions

Two low band gap polymers CDM and BDT, which are based on the carbon-bridged dithienyl structure have been simulated by density functional theory and semiempirical methods. The long wavelength features in the absorption spectra of the molecules which we relate to the $\pi-\pi^*$ transitions are in good agreement with experimental ones. Our results show an extensive conjugation in the present system. Taking the maximum theoretical absorption as the energy gap, the corresponding band gaps are 1.28 and 1.74 eV for PCDM and PBDT, respectively. The experimental ones are 1.28 and 1.73 eV for PCDM and PBDT, respectively.

The B3LYP/6-31G, PM3 and AM1 calculations indicate that all conformers adopt a planar configuration with individual monomers adopting either a parallel or antiparallel configuration with equal probability.

Table 2

Theoretically calculated energies of the $\pi-\pi^*$ transitions in monomers, dimers, trimers, tetramers and pentamers of CDM and BDT compared with those estimated from experimental UV-visible absorption spectra [26,27]

Material	Monomer cal. (eV)	Dimer calc. (eV)	Trimer calc. (eV)	Tetramer calc. (eV)	Pentamer calc. (eV)	Experimental polymer (eV)
CDM	1.76	1.57	1.39	1.30	1.28	1.28
BDT	2.58	2.13	1.91	1.76	1.74	1.73

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