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Chromophores of neutral and dicationic thiophene-based oligomers − A study by first-principle methods

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Dedicated to Prof. Dr. Nikolai Tyutyulkov on the occasion of his 80th birthday.

Abstract

Time-dependent density functional theory (TD-DFT) and semiempirical methods (ZINDO-CIS, PPP-CIS) were applied to colored neutral and dicationic thiophene-based oligomers; in addition to the parent oligothiophenes and various α,α'-end-capped derivatives, oligothiophenes with thiophene rings linked by methine, vinylene or phenylene groups were studied. Being π-chromophores, the compounds absorbed intensely in the Vis−NIR region; variation of the absorption energy with the reciprocal of the number of thiophene rings resulted in low band gap (as is known for low band gap polymers). Whilst the parent oligothiophenes displayed no singlet/singlet instability up to the octadecithiophene, the long chain oligomers were singlet/triple unstable. According to BS-UDFT calculations, biradical oligomers (two-plarons) were slightly favored over conventional dications (bipolarons). The color-determining electronic transitions of large size oligothiophenes calculated by open shell TD-DFT were little shifted in energy relative to those calculated using closed shell TD-DFT. The electronic structure of the oligomers is discussed in terms of bond length alternation and nucleus-independent chemical shifts.

Keywords: Neutral and dicationic oligothiophenes; Bridged thiophene dications; Density functional and time-dependent density functional theory calculations; Spin-restricted and spin-unrestricted Kohn−Sham calculations; Molecular and electron structure; Nucleus-independent chemical shift; Electronic excitation; Visible and near infrared absorption

1. Introduction

Chromophores of small- and middle-size conjugated compounds have been widely studied in the past. The results have been summarized in textbooks and monographs [1]. Because of the various potential applications there is a recent interest in NIR chromophores [2]. The monocationic polymethine dyes (cyanine dyes) constitute one important class of dyes that absorb beyond 750 nm at long chain lengths [3]. Absorption maxima up to 1600 nm have been reported [4]. These compounds belong to the $\pi\pi^*$-chromophores. However, a peculiar behaviour has been observed for these dyes at long chain lengths [5,6]. The sharp intense ‘‘color band’’ disappears in favor of a lower intense and structureless absorption band. According to quantum chemical calculations the characteristic bond length equalization of the polymethines is lost and a more localized bond system evolves with essentially single or double bonds. The localization of the bonds was discussed in terms of symmetry breaking [6].

Conjugated dications represent another and less-well studied class of charged conjugated compounds displaying intense NIR absorptions. These chromophores were encountered in studies on electric conductivity by doping of π-conjugated oligomers and polymers (cf. Ref. [7]). Compounds such as oligothiophenes were studied for optoelectronic and microelectronic applications [8]. The neutral compounds easily undergo oxidation forming singly, doubly or higher oxidized species. In contrast to the singly oxidized radical oligothiophenes (called positive polarons in solid states physics) doubly

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oxidized compounds (bipolarons) are spinless. As is well known, dicationic bipolarons play the dominant role in polythiophene charge storage excitations at high dopant concentrations [9]. Dications are also generated by oxidative chemical doping in solution and were recorded in electrochemical studies such as cyclovoltametry combined with in situ Vis–NIR spectroscopy. Like monocationic polymethine dyes dicationic oligomers are closed shell systems displaying intense low-energy $\pi \rightarrow \pi^*$-transitions. Because of their stretched structure the transitions show very large absorption intensity at long chain lengths.

However, because of the presence of two charges in a single conjugated molecule the electronic structure may behave exceptionally. Either the charge is more uniformly distributed over the entire molecule or the two charges tend to partially separate. The latter case is expected for larger molecules. If a separation of charges occurs the electronic structure is getting biradicaloid or biradicalic. The biradicaloid nature of the dication is revealed by singlet/triplet instability. Geometry optimization with spin-unrestricted DFT leads to a two-polaron (also called polaron-pair) structure that differs from the conventional structure described by spin-restricted DFT [10]. The formation of bipolarons and two-polarons was examined theoretically [11–13] and experimentally [7]. For medium-size oligothiophene dications the two-polaron state increasingly contributes to the electronic ground state description. Whereas at short chain lengths the bipolaron is energetically favored relative to the triplet state, singlet and triplet state are predicted to be degenerate at long chain lengths [11].

The goal of this study is to calculate spectral absorption data of oligothiophenes by time-depended density functional theory (TD-DFT) at the spin-restricted and spin-unrestricted Kohn–Sham level. First the question is asked whether neutral oligothiophenes may exhibit a deep color. The main interest, however, is directed to the study of the electronic excitation of dicationic species. Knowledge about excitation energies of different chain lengths will also afford information about the band gap of polymers at infinite chain length.

2. Choice of the chromophoric compounds

Neutral oligothiophenes have been extensively studied [14]. The quaterthiophenes **1–4** were selected as test cases for neutral oligomers. They are classified as class-1 type compounds in Scheme 1. The parent structures are shown in frames. The resonance formulas of **1–4** suggest weak bonds between the thiophene rings. As discussed below benzannelation of **1** to the isothionaphtene oligomer **2** significantly changes the spectral properties of the parent compound [15]. Substitution of oligothiophenes with electron-withdrawing substituents in the terminal α,α'-position led to deeply colored compounds [16–18]. A derivative of **3** serves as an example for acceptor-substituted oligomers [17]. Another series of oligomer consists of push–pull substituted compounds [19,20] end-capped by amino and cyanvinyl groups such as **4a**. Structure **4b** contains the simpler carbonyl acceptor group. An outstanding case is compound **4c**. It exhibits a cyanine-type backbone. In contrast to **4a** and **4b** the tetramer **4c** is a cation with two amino groups in the terminal positions. The polymethine-type backbone structure should result in essentially delocalized CC-bonds.

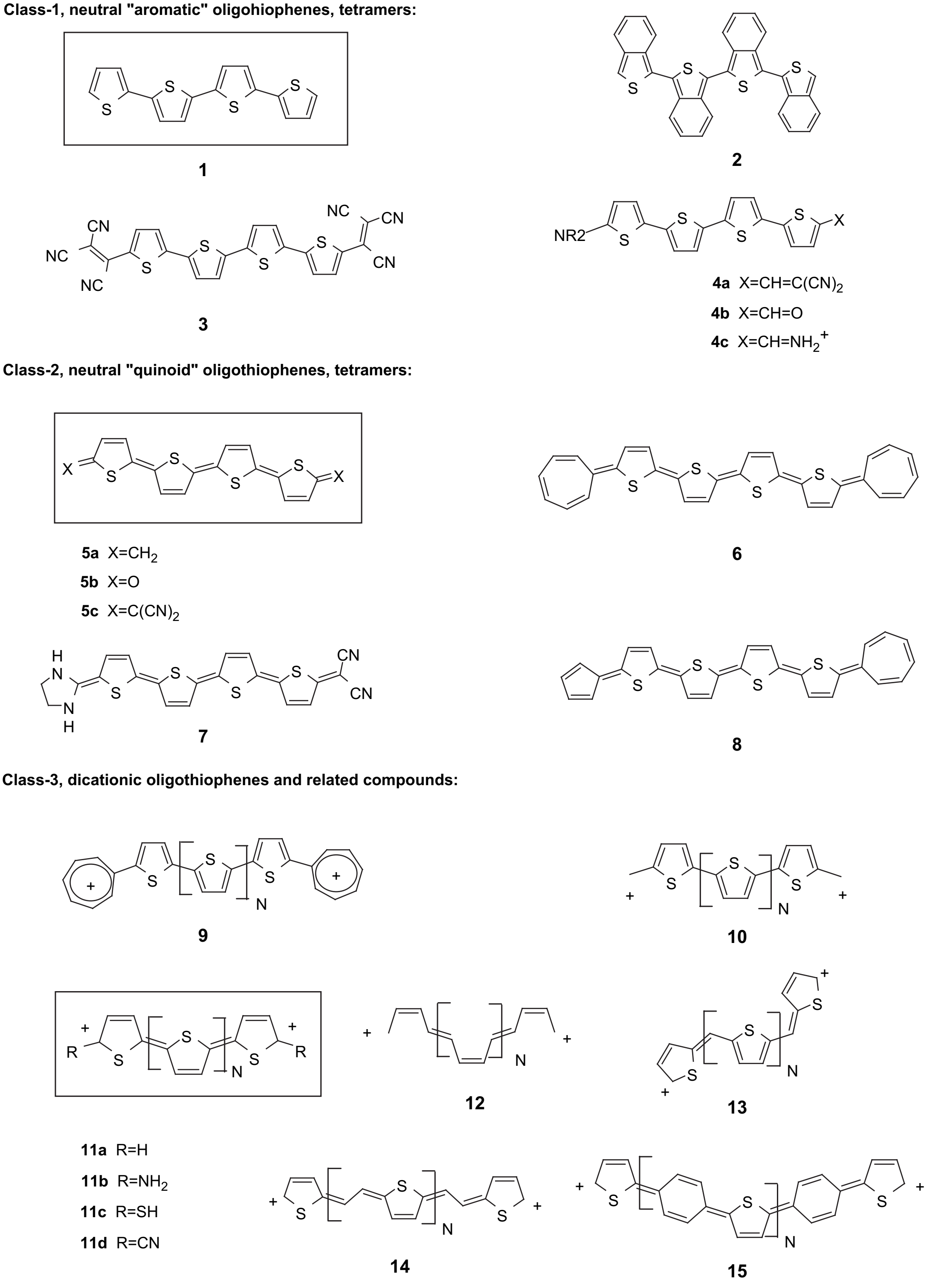
In contrast to class-1-type compounds quinoid bond fixation should determine the structures **5–8** of Scheme 1 (class-2-type compounds) except for bis(cyanomethylene)oligothiophenes **5c** [21–24]. Compounds of this series are not yet known. Because of the bathochromic shift of the color band to the NIR region there are compounds that are no longer colored but rather faint gray in solution [23]. The question has been asked [22] whether strongly electron-withdrawing substituents may model chromophores of doubly oxidized oligomers. In the more extended quinoid structure such as **6** the end groups are conjugated rings. In turn, the chain may be terminated by a donor and an acceptor group giving rise to push–pull-type oligomers. One encounters this type of structure with **8**. Alternatively the oligomer **8** may be written as zwitterionic structure with the charged terminal groups tropylium and cyclopentadienide. The contribution of this resonance structure suggests a lowering of the quinoid character because of electron delocalization.

Bistropylium end-capped compounds such as **9** [25] may be considered as transition cases between class-2-type and class-3-type oligomers (Scheme 1). According to the resonance formula in Scheme 1 dication **9** appears as an acceptor-substituted aromatic compound related to **3**. Salts of the dimer, trimer and tetramer of **9** were isolated as violet to black powders. If the terminal tropylium groups of **9** are truncated to methinium groups the structure **10** emerges.

We have studied the basic series of the dicationic oligomers **11a** with chains between 4 and 18 thiophene rings. Knowledge about spectral data of the parent compounds **11a** is scarce. Except for parent compounds of chain lengths $N = 6$ and 8 generated in solution [26–28] or in zeolite ($N = 4$, 6, 8 and 9) [29,30] spectral data are known for oligothiophene dications substituted by aliphatic or aromatic residues [31–35]. Spectral data are also available for end-capped diphenylamino- [36] and mesitylthio-oligothiophene dications [37]. Oligothiophene dications may be viewed as polyene dication with sulfur bridges. Complete extraction of sulfur from the parent oligothiophene dications leads to the oligoene dications of the structure **12**. These basic structures were calculated for comparison.

Compounds of other series of thiophene-based π-conjugated oligomers dications examined in this study contain linking groups between thiophenes in α,α'-position, such as methine in **13** [38], vinylene in **14** [39–41] and phenylene in **15**. Incorporation of the methine linkages within the conjugated chain has been investigated as a possible route to low-gap polymers [8,38]. Vis–NIR data and theoretical results are available for oligo(thienylenevinylene) dications **14**, which display extremely long absorption wavelengths. To the best of our knowledge the more extended oligo(thienylenephenylene) dications **15** are not yet known.

For simplicity, all the structures **1–15** were formulated by single resonance forms. A single formula cannot sufficiently



Scheme 1.

well reflect the real bonding and charge distribution. The sulfur atoms above all will carry a considerable part of the charge. The heteroaromatic or heteroquinoid formulas in Scheme 1 depict idealized bond features. The formula description implies that the single–double bond alternation of the dications exhibits the reversal pattern of the bonds of neutral compounds.

3. Computational methods

To calculate ground state geometries and excitation energies the Kohn–Sham-density functional theory (DFT) and time-dependent DFT (TD-DFT) were employed [42]. In these methods the interaction of the many-electron problem is replaced with the effective single-particle problem that can be solved much faster than by *ab initio* quantum chemical calculations. TD-DFT is the most prominent method for calculation of spectral data of medium-size and large molecules at present [43]. The Becke3–Lee–Yang–Parr functional (B3LYP) and the parameter free Perdew–Burke–Enzerhof functional (abbreviated by PB0 or PBE1PBE) employed in this study are the most widely used exchange-functionals in DFT and TD-DFT calculations, such as in calculating electronic transitions of sulfur-containing dyes [44,45]. The results obtained by both of the functionals are closely similar [46].

The economical 3-21G split-valence basis set augmented by a set of d-functions is preferred in this study, because further extension of the basis set did not lead to significant changes in the calculated absorption wavelengths. Some calculations with extended basis sets are mentioned to justify this conclusion. The calculated electronic transitions are vertical transitions that should approximately correspond to experimental band maxima.

DFT calculations were carried out with the spin-restricted RDFT method for closed shell and with the spin-unrestricted UDFT method for open shell systems. Mixing of HOMO and LUMO orbitals may destroy the α/β-spatial symmetry in the initial guess resulting in spin-broken symmetry (BS) solutions. Unrestricted DFT (UDFT) is frequently used for the description of open shell singlet biradicals [47,48]. The ground state energy of the dications calculated by BS-UDFT may be lower than calculated by RDFT [10,11]. The biradicaloid character of the lowest-energy electronic state obtained by UDFT was established by CASSCF with the number of electrons larger than zero outside the closed shell bonding orbitals [13]. Vis–NIR spectral data were calculated by time-dependent DFT (TD-DFT). For comparison spectral data were also calculated by the semiempirical PPP-CIS method (π-approximation) [49] and by the ZINDO-CIS method (all-valence electron approximation) [50] taking into account 15×15 and 10×10 singly excited configurations, respectively. DFT, TD-DFT and ZINDO-CIS (“ZINDO/S”) calculations were performed by the GAUSSIAN03 program package [51], and PPP-CIS (“PPP”) by WPSIN5f [52].

4. Results and discussion

4.1. Neutral compounds

As well known the thiophene rings of the neutral parent oligothiophenes are in *trans* conformation with respect to each other, called “*all-anti*” in the following. They are slightly distorted in the oligomer. The stabilization energy is low. For the tetramer **1** it is less than 0.1 kcal/mol with respect to the fully planar structure is. A large distortion is calculated for the tetramer of **2** with a dihedral angle of about 46° between two adjacent benzo[c]thiophene rings. The energetic stabilization energy of the sterically crowded **2** relative to the hypothetical planar structure amounts to 7.9 kcal/mol.

The resonance formulas of Scheme 1 suggest that class-1 oligothiophenes exhibit a pronounced bond length alternation (BLA: whereby BLA indices of the thiophene rings were defined as $(R_{23} + R_{45})/2R_{34}$). BLA indices lower than 1 indicate thiophene-like substructures. These are thienobenzoid structures. The chain structure is characterized by long inter-ring bonds in that case. The thiophene units preserve to a considerable extent their independence with a predominantly local cyclic π-delocalization. The delocalized nature of the individual rings is best evaluated by nucleus-independent chemical shifts (NICS). The NICS index is a simple and useful aromaticity index devised by von Ragué Schleyer et al. several years ago [53]. This index is based on the magnetic property of the compound and defined as the negative of the isotropic magnetic shielding constant at the origin of the coordinate system of the rings. The lower the values of the NICS index the stronger the cyclic electron delocalization (“aromaticity”) of the ring.

BLA and NICS values of representative tetramers of the class-1 to class-3 series are collected in Fig. 1. The lengths of the inter-ring bonds value determine the extent of the interannular coupling. The NICS values of the oligothiophene **1** do not differ much from the isolated thiophene (−12.9 ppm). The BLA values of the rings are lower than 1 and the inter-ring bonds relatively large. Thus, the oligomer is thienobenzoid. In contrast, the neutral tetramer **5a** of the class-2 series is thienoquinoid. The NICS indices are considerably larger than those of **1** but do not reach the NICS value of the 2,5-(bismethylene)-3,4-dihydrothiophene as the reference compound (−5.9 ppm) (cf. Fig. 1). The BLA values are now larger than 1 and the inter-ring bonds are relatively short. The resonance formulas of Scheme 1 are essentially in harmony with the theoretical results. The dicationic tetramer of the class-3 type of series **11a** displays similar structural characteristics as **5a** as discussed below.

A change towards bond length equalization is found in passing from **1** to **3**. The inter-ring bonds, however, have single bond character in these structures. The thienobenzoid character is reduced in push–pull substituted compounds such as **4a** and **4b**. According to BLA values of 1.00 and 1.01 and inter-ring bond lengths of about 1.41 Å the polymethine-type tetramer **4c** displays marked bond delocalization along the chain inter-ring CC-bonds confirming the close relatedness of this structure to polymethine-type dyes.

Spectral data of three neutral quaterthiophenes **1–3** and of a related tetramer with tropylium substituents (**9**) are presented in Fig. 2. The absorption wavelength of 415 nm of the parent tetramer **1** calculated with the 3-21G* basis agrees satisfactorily well with the experimental value (399 nm [54]). The calculated absorption wavelengths are less dependent on the functional. The deviations between the spectral data of the B3LYP and BP0 calculations are less than 0.1 eV. The more common B3LYP functional was preferably used in the following calculations. Calculations of the tetramer with extended basis sets resulted in bathochromic shifts (3-21+G*, 443 nm, and 6-31+G*, 455 nm). The agreement between theory and experiment is not improved relative to the 3-21G* basis set. TD-DFT calculations are highly superior to RHF-CIS *ab initio* calculations which provided considerably too short absorption wavelengths (338 nm for **1**) whereas the expensive *ab initio* calculation at the CASPT2 level provided a relatively large value with 452 nm [55].

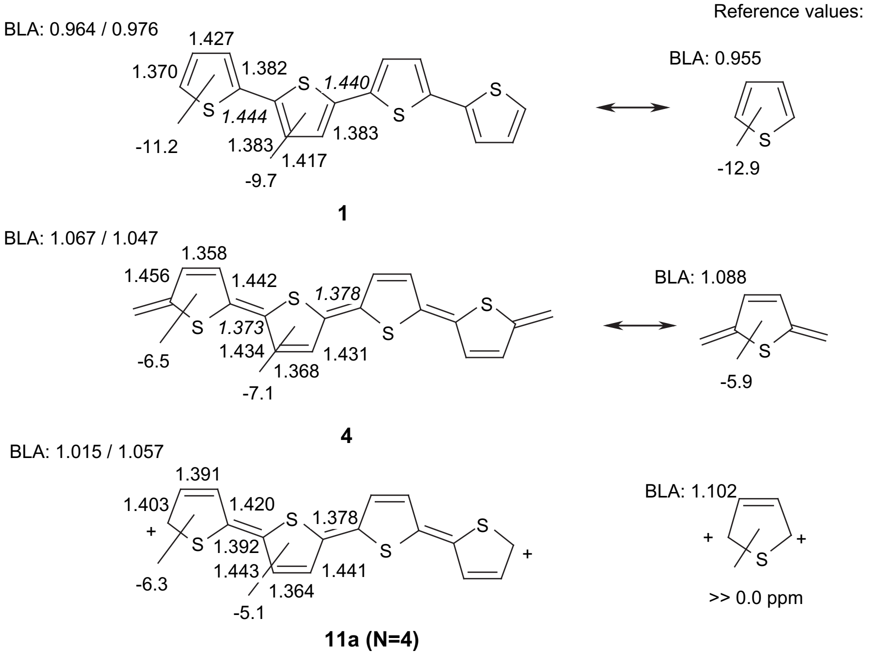
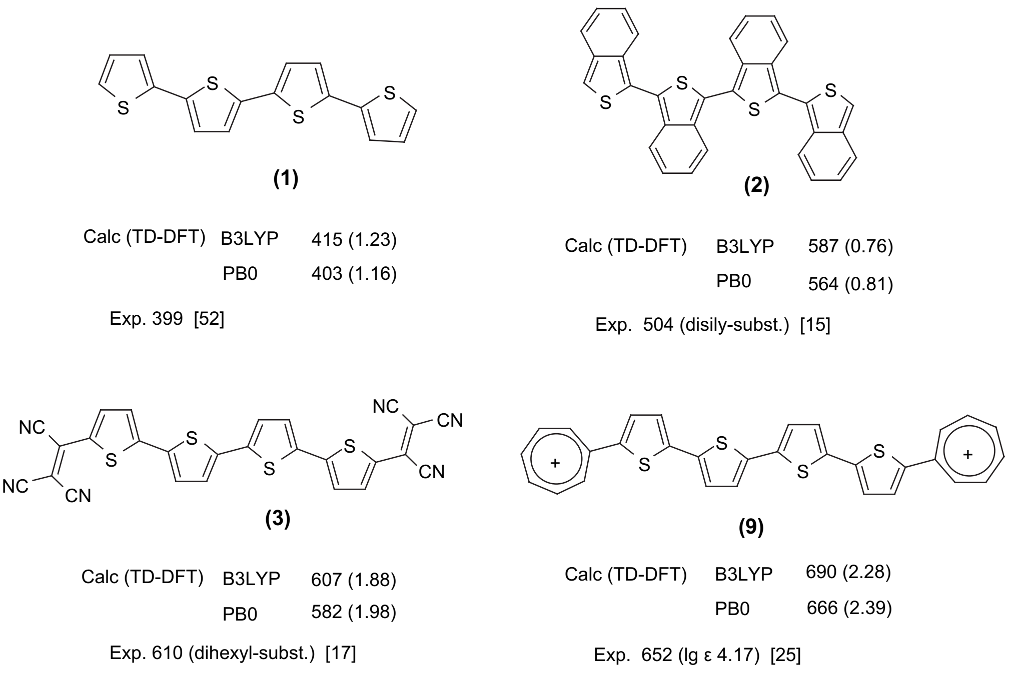


Fig. 1. Bond lengths in Å and nucleus-independent chemical shift indices (NICS) in ppm of selected compounds. The BLA values are bond length alternation indices.

The benzannelated parent tetramer **2** is not known. The molecule is predicted to be twisted. According to the TD-DFT calculation **2** absorbs at about 150 nm longer wavelengths than **1**. The disylated isothianaphtene tetramer actually absorbs at significantly longer wavelengths than the parent tetramer (504 nm) [15].

More strongly bathochromic shifts are caused by acceptor substituents in the α,α'-positions. The α,α'-tricyanovinylene end-capped **3** with two additional hexyl-substitutents attached to the thiophenes absorbs at 610 nm [16]. This agrees well with wavelength predicted by the TD-DFT (cf. Fig 2). The longest wavelength absorption of the push–pull substituted **4a** with the substituent NR_2 = piperidino was calculated at 673 nm. An oligomer of this series is known with the dimer [19]. The compounds **4b** and **4c** with merocyanine- or cyanine-type backbones are predicted to absorb intensely at 529 and 715 nm. The bond delocalized structure **4c** is not only reflected in the large absorption wavelength but also in the high absorption intensity.

The quinoid tetramers **5a** and **5b** are predicted to absorb at about 600 nm (**5a**: 637 nm and **5b**: 613 nm) whereas the



(1)
Calc (TD-DFT) B3LYP 415 (1.23)
PB0 403 (1.16)
Exp. 399 [52]

(2)
Calc (TD-DFT) B3LYP 587 (0.76)
PB0 564 (0.81)
Exp. 504 (disily-subst.) [15]

(3)
Calc (TD-DFT) B3LYP 607 (1.88)
PB0 582 (1.98)
Exp. 610 (dihexyl-subst.) [17]

(9)
Calc (TD-DFT) B3LYP 690 (2.28)
PB0 666 (2.39)
Exp. 652 (lg ε 4.17) [25]

Fig. 2. Calculated and experimental absorption wavelengths of selected tetramers in nm calculated by B3LYP and PB0 functionals (3-21G* basis set).

tetracyanovinyl-substituted **5c** is significantly more bathochromic (724 nm). Chromphores of the latter are well known [21–24]. An absorption band at about 790 nm has been recorded for a derivative of the neutral tetramer **5c** [23]. The absorption maximum of the substituted hexamer has been found at 1372 nm in solution with a tail of the absorption band up to 1600 nm [39].

The quinoid tetramers of the structure **6** and **8** should absorb intensely at more than 800 nm. The intense absorptions, however, do not originate from a single intense low-energy transition. One or two weak or forbidden transitions have lower transition energies than the intense transition.

4.2. Dicationic compounds

The planar tropylium end-capped tetramer **9** belongs to a series of oligomers that appear exceptional among the dications. The nearly planar tetramer displays characteristics of both charged and neutral oligomers. According to the Mulliken population analysis about half of the charges of the end groups are transferred to the tetramer chain resulting in a partially positive charged tetramer fragment. On the other hand, approximate CC bond length equalization (BLA about 0.99) indicates predominant aromatic character. The heteroaromatic character is supported by strongly negative NICS values of the thiophene rings. The NICS indices are close to the neutral parent quaterthiophene **1**. The same feature holds for higher members of the series **9** calculated up to $N = 9$.

In accord with the calculated and measured absorption data [25] of **9** ($N = 2$) in Fig. 2 the tetramer is deeply colored with an intense absorption at about 650 nm. The result of the TD-DFT calculation agrees well with the experimental finding. Based on the DFT optimum geometry the PPP-calculation provides 681 nm using standard parameters [52]. The long wavelengths absorption does not originate from an intrinsic intramolecular CT-transition. Examination of the electron population at the PPP level revealed that 0.38 electrons altogether are transferred from the quaterthiophene fragment to the two terminal tropylium groups on excitation. The relatively weak CT enables TD-DFT to be used whereas the method grossly fails in calculating real CT transitions [43]. The spectral effect of acceptor substitution is due to the strong stabilization of the LUMO in which the acceptor groups largely participate.

Replacement of the terminal tropylium by methinium leads to the parent structure **10**. With this structural change the electronic structure is also changed: the CC-bonds of the terminal thiophenes have quinoid character whereas the CC-bonds of the inner thiophene rings are smoothed out, similarly to the case **9**. The inter-ring bonds of both **9** and **10** have essential single bond character. These bonds become increasingly shorter with inceasing chain lengths. Compounds of series **10** are less bathochromic than **9** compared at the same chain length. Nevertheless, the absorption wave lengths of nonithiophene of this series are predicted by TD-DFT at about 1000 nm (Fig. 3).

The oligothiophene dications of series **11a** are prototype compounds of thiophene-based oligomer dications. The planar compounds have either point group C_{2h} (with an even number of rings) or C_{2v} (odd number of rings). Independent of the chain length the BLA values are larger than 1 whereas the inter-ring bonds are relatively short (Table 1). The dications have essentially quinoid character and hence the aromatic character of the neutral compounds is lost with the twofold ionization of the neutral oligothiophenes. The quinoid character is most prominent in the central part of the chain. This finding agrees with X-ray diffraction studies of a substituted dicationic tetramer [31].

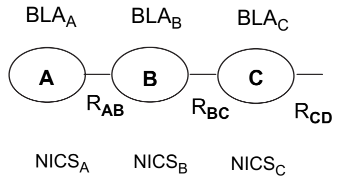


Fig. 3. Fragmentation mode of the oligothiophene chain and abbreviations used in Table 1.

Data about the bond characteristics of parent dications **11a** of different chain lengths are collected in Table 1. The nature of the structure is supported by the calculated isotropic NICS indices. These values are significantly larger than those of the neutral compound **1** with an essentially aromatic substructure. However, strongly decreasing NICS indices in series **11a** with increasing chain length signalize an increasing aromatic character of the thiophene fragments. The NICS value of the terminal thiophenes decrease from −0.1 of the dimer to −8.7 ppm of the heptamer. Concomitantly the BLA values decrease from 1.058 to 0.992. Principally the same conclusion was drawn earlier from calculated molecular geometries [56]. Thus the resonance formula **11** of Scheme 1 cannot adequately reflect the real bonding of all members of the series.

Dications exist in the *all-anti* conformation like the neutral precursors. This is exemplified with the pentamer **A** in Fig. 4. According to the calculations the stretched *all-syn* conformation **B** is energetically disfavored by about 2 kcal/mol over the bent *all-trans* conformation. Because the *all-syn* isomer exhibits an electric dipole moment the energy difference may be lowered by environmental effects. However, the stabilization energy of the *all-anti* conformation increases with the chain length. On the other hand, because of the enhanced double bond character of the inter-ring bonds the barrier to isomerization of the dications is strongly enhanced relative to the corresponding neutral compounds and consequently the isomerization made difficult. The transition energy was calculated to 27.6 kcal/mol for the tetramer dication [31]. At any rate, X-ray diffraction studies of the salts of two substituted oligomer dications are in favor with the *all-anti* conformation of dications [31].

TD-DFT and semiempirical calculations of the *all-anti* configured parent compounds **11a** predict a single color-determining electronic transition at long wavelengths. The intense low-energy A_g–B_u transitions (even number of thiophene rings) and A_1–B_2 transitions (odd number of thiophene rings) are strongly dipole-allowed polarized along the long axis of the molecule. These transitions are essentially single-particle

Table 1
Dependence of bond length alternation (BLA) indices of inter-ring bond lengths in A and nucleus-independent chemical shifts (NICS) indices in ppm of dications on the number N of thiophene rings of the chain (B3LYP/3-21G*)

Compound	N	BLA_A	BLA_B	BLA_C	R_{A-B}	R_{B-C}	R_{B-C}	$NICS_A$	$NICS_B$	$NICS_C$
9	3	1.000	0.991		1.434			−7.6	−9.1	
	4	1.004	0.992		1.429	1.436		−7.5	−9.1	−9.0
	5	1.009	0.995	0.989	1.424	1.434		−7.4	−9.0	−9.1
	7	1.014	1.000	0.990	1.418	1.429	1.435	−7.3	−8.8	−9.1
10	3	1.048	1.004		1.431			−5.9	−8.4	
	4	1.055	1.006		1.417	1.436		−5.9	−8.3	
	5	1.059	1.012	0.996	1.407	1.431	–	−5.9	−8.1	−8.8
	7	1.062	1.020	1.000	1.397	1,420	1.432	−5.9	−7.8	−8.6
11a	1	1.102	–	–	–	–	–	(+118.9)*		
	2	1.058			1.36	–	–	−0.1		
	3	1.030	1.072		1.379	–	–	−4.3	−3.8	
	4	1.015	1.057		1.392	1.378	–	−6.3	−5.1	
	5	1.004	1.044	1.053	1.402	1.384		−7.5	−6.3	−5.8
	6	0.997	1.034	1.045	1.409	1.391	1.387	−8.2	−6.6	−6.3
	7	0.992	1.025	1.037	1.414	1.397	1.392	−8.7	−7.0	−6.8
13	3	1.022	1.010		–		–	−5.5	−8.3	
	5	1.002	1.027	1.061	–	–	–	−7.5	−8.0	−5.7
	7	0.994	1.035	1.053				−9.5	−7.2	−6.8
14	3	1.021	1.067		–	–	–	−6.2	−4.4	
	4	1.006	1.055					−7.9	−5.7	
	5	0.997	1.043	1.052	–	–	–	−8.9	−6.6	−6.3
15	3	1.005	1.045		–	–	–	−6.4	−5.0	
	4	0.992	1.026					−7.7	−6.1	
	5	0.985	1.014	1.015	–	–	–	−8.4	−6.7	−9.3

For the fragmentation mode see Fig. 3.

transitions that involve mainly the frontier Kohn–Sham orbitals of the $\pi \rightarrow \pi^*$-type. This implies that the simple PPP π-model can be applied. The absorption energy calculated for the longest considered chain (**11a**, $N = 18$) amounts to 0.45 eV at the TD-DFT. The next shorter transition is calculated at 0.72 eV (A_g–A_g transitions) and is dipole-forbidden. An additional allowed A_g–B_u transition following at 0.88 eV is weak. The next intense A_g–B_u transition appears at 1.75 eV ($f = 3.53$).

The calculated spectral data of parent oligothiophene dications are listed in Table 2. For comparison, results of ZINDO-CIS and PPP-CIS calculations were added. In color chemistry spectral data are commonly given in wavelengths. However, the corresponding energies are preferred for comparison. The wavelength scale is strongly expanded in the NIR region and results in wavelengths cannot give a realistic view about the performance of the theoretical models.

According to Table 2 TD-DFT and semiempirical ZINDO-CIS and PPP-CIS calculations of oligothiophene dications display intense electronic transitions in the NIR at relatively short chain lengths. In analogy to other homologous series of conjugated compounds, the first transition energy is decreasing with increasing chain length. If one uses the term ‘‘thienylene shift’’ in analogy to the ‘‘vinylene shift’’ of cyanine dyes the shift of the oligophene parent cations increases from 100 nm at shorter chain lengths to 200 nm at longer lengths (up to $N = 18$). The comparison of the theoretical results shows that the absorption wavelengths predicted by TD-DFT and ZINDO-CIS are in surprisingly close numerical agreement. However, the calculated transition energies are systematically larger than the experimental excitation energies. The deviation declines with increasing chain length. The error is 0.61 eV for quaterthiophene (**11a**, $N = 4$) and it amounts to 0.28 eV for nonithiophene ($N = 9$). PPP transition energies are less in error and the deviation for nonithiophene amounts to 0.03 eV only. This is certainly due to a fortunate cancellation of errors. A reliable evaluation of the theoretical results is difficult because of the limited experimental data of the parent structures. The data listed in Table 2 are heterogeneous and may also be shifted by environmental effects.

To better know the deficiencies of the theoretical models two experimentally well characterized dications were selected and chosen as test cases. Along with other compounds the structurally rigid bicyclo[2.2.2]octa-annelated tetramer **16** was synthesized by Komatsu et al. [31] as a deep blue salt with the $(SbF_6^-)_2$ counter anions. The color is green in solution. This dication contains a nearly planar quaterthiophene backbone and has C_{2h} symmetry. The longest wavelength intense absorption maximum of this compound was recorded at 788 nm corresponding in energy to 1.57 eV. On the other hand, Fichou et al. [27] generated unsubstituted hexamer dication **11a** ($N = 6$) quantitatively by stepwise oxidation of the neutral sexithiophene in solution. The maximum of the absorption band was recorded at 1003 nm (1.24 eV). The experimental excitation energies of 1.57 and 1.24 eV of the two compounds can be compared with the TD-DFT transition energies of 1.98 and 1.61 eV, respectively, at the TD-DFT level (3-21G*). Thus the deviation between theory and experiment amounts to nearly 0.4 eV. The relatively error contrasts with the mean absolute deviation of smaller sulfur-containing organic compounds, which is only half as large [55]. A more extended basis set such as 6-31G* did not provide better results (cf. Fig. 5). Astonishingly, the parametrized – ZINDO-CIS

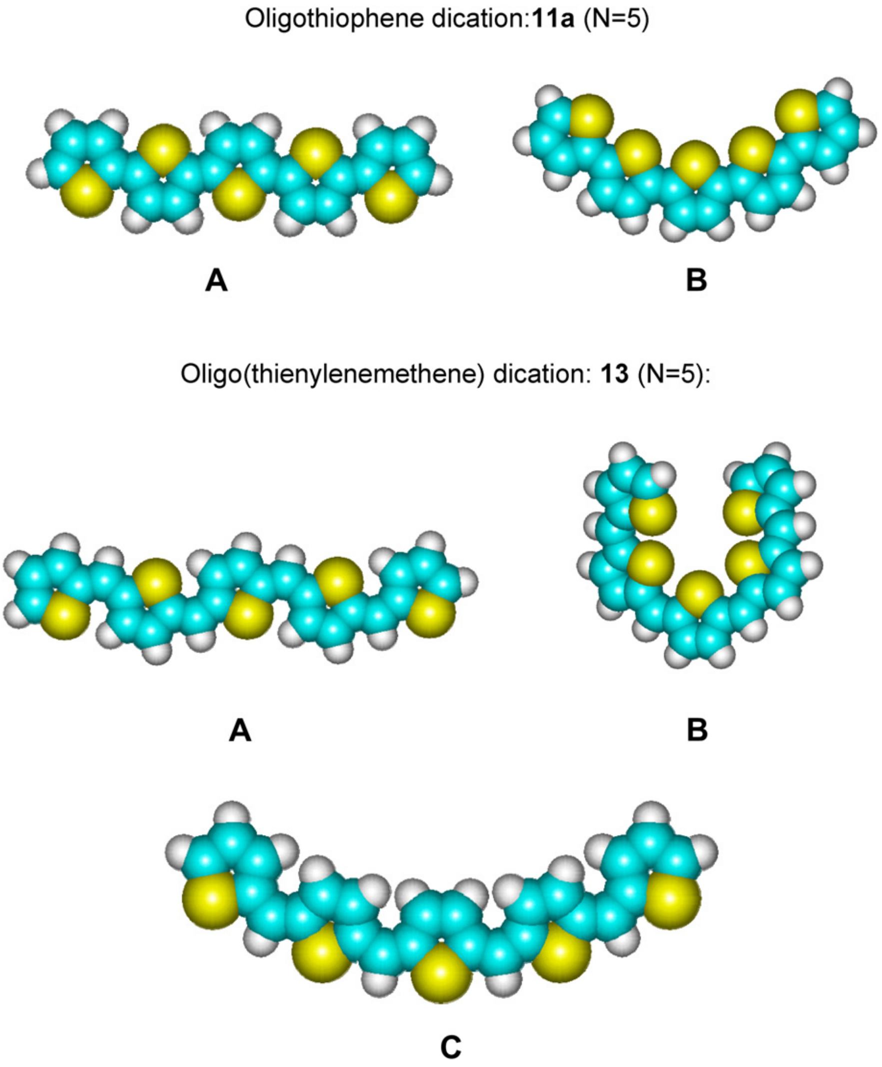


Fig. 4. Isomeric parent and methine-bridged quinquethiophenes.

calculations based on a completely different theoretical model provided principally the same error as TD-DFT. Additional experimental data, in particular of larger size oligomers, may help to confirm and understand the relatively large but nearly constant deviations between theory and experiment.

The absorption intensity was evaluated by the dimensionless oscillator strength *f*. The *f*-values of rod-like polymer increase strongly with the chain length. Values up to $f = 7$ were calculated by TD-DFT. The *f*-values of the dications are definitely larger than those of the neutral compounds. Experimental values are not yet known. Measurements of molar absorption coefficients ε of terminally substituted thienylpolyenes only revealed that dications absorb in fact with approximately twice the intensity of the neutral compounds [57]. A high experimental log ε-value of 5.65 was reported with a chain of nine CC-double bonds in the last mentioned series.

Remarkably, *f*-values in the oligothiophene dication series calculated by TD-DFT did not continue increasing in some series at long chain lengths but rather decreased (cf. Table 1). This trend is certainly due to the fact that the oscillator strength contains two components, the square of the transition moment M^2 and the transition energy ΔE. Since ΔE drops with the chain lengths this change may overcompensate the increase of M^2. This interpretation is supported by finding that the M^2 exhibits a continuous increase with the chain lengths.

Spectral data of α,α'-end-capped oligothiophenes are listed in Table 3 along with the data of the parent compounds. The first absorption undergoes bathochromic shifts with electron releasing groups such as NH_2 and SH and hypsochromic shifts with the electron-withdrawing group CN. As long as short chain lengths are considered SH in **11c** is more auxochromic than NH_2 in **11b**. We have recently reported spectral data of α,α'-diphenylamino-end-capped oligothiophenes [36]. For instance, the diphenylamino end-capped pentamer aborbs at 1201 nm. The TD-DFT calculation resulted in 963 nm. Again the absorption wavelength is underestimated. The deviation of 0.26 eV is slightly lower than in the above mentioned cases.

If the sulfur atoms are fully removed from the oligothiophene chain the heteroatom-free conjugated dication **12** is obtained. Although the vinylene shift is low with 50 nm compounds of moderate chain lengths should also NIR chromophores. NIR absorption maxima are expected for chains with

Table 2
Calculated transition energies and respective *f*-values (in parentheses), and absorption wavelengths λ of the lowest-energy transitions of parent oligothiophene dications **11a** (TD-DFT B3LYP/3-21G*)

N	TD-DFT[a]				ZINDO-CIS		PPP-CIS[b]		Exp.	
	6-31G*[c]		3-21G*						Solution[d]	Zeolite[e]
	ΔE (*f*)	λ	ΔE(*f*)	λ	ΔE(*f*)	λ	ΔE(*f*)	λ	ΔE	ΔE
4	2.18 (1.44)	569	2.19 (1.40)	566	2.12 (2.15)	585	1.70 (2.46)	731	1.57	
5	1.85 (2.08)	670	1.86 (2.10)	665	1.83 (2.58)	684	1.41 (2.28)	870	1.30–1.38	
6	1.60 (2.64)	775	1.61 (2.67)	769	1.59 (2.70)	779	1.22 (4.15)	1016	1.02–1.31	1.22
7	1.40 (3.13)	884	1.41 (3.17)	878	1.42 (3.32)	873	1.06 (4.91)	1165	1.01	
8	1.24 (3.55)	1000	1.25 (3.58)	995	1.28 (3.64)	970	0.95 (5.73)	1311	0.82–0.89	0.90
9	1.10 (3.88)	1125	1.11 (3.92)	1121	1.16 (3.92)	1073	0.85 (6.67)	1444	0.82	0.86
10	0.98 (4.12)	1263	0.98 (4.12)	1261	1.05 (4.16)	1186	0.79 (8.05)	1560		
11	0.88 (4.24)	1416	0.88 (4.24)	1415	0.95 (4.37)	1309	0.75 (9.64)	1664		
12	0.78 (4.31)	1581	0.78 (4.28)	1582	0.86 (4.53)	1445	0.71 (11.73)	1735		
13	0.71 (4.33)	1754	0.71 (4.30)	1756	0.79 (4.67)	1579				
14	0.64 (4.30)	1941	0.64 (4.27)	1944	0.72 (4.77)	1727				
15	0.58 (4.27)	2134	0.58 (4.24)	2137	0.66 (4.86)	1872				
16	0.53 (4.24)	2332	0.53 (4.21)	2335	0.62 (4.94)	2013				
17	0.49 (4.21)	2537	0.49 (4.18)	2540	0.58 (5.01)	2153				
18	0.45 (4.19)	2744	0.45 (4.16)	2447	0.54 (5.08)	2281				

[a] The spectral data of first intense absorptions of the first two members are $N = 2$: 3.95 eV, 313 nm, $f = 0.58$ and $N = 3$: 3.03 eV, 409 nm, $f = 0.83$. In contrast to the following members of the series they are not transitions of lowest-energy.

[b] No convergence at $N > 12$.

[c] Single point calculations: TD-DFT B3LYP/6-31G*//B3LYP/3-21G*.

[d] The given range of values includes both spectral data of unsubstituted dications [26–29] and data of compounds substituted by aliphatic or phenyl groups [31–35].

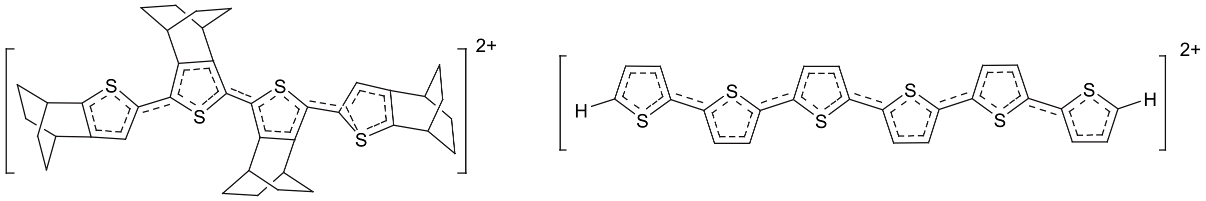
[e] For the experimental data see Ref. [29].

more than 14 double bonds. Oligoene dications with end-capped thienyl groups and 9 double bonds absorb with high intensity at about 1000 nm [57]. As exemplified in a footnote of Table 3 the difference in the absorption wavelength between **12** (C_{2v} or C_{2h}) and the isomeric *all-s-cis* structures (C_{2h}) is low.

4.3. Bridged thiophene-based dicationic oligomers

The oligomers **13–15** contain conjugated groups that are inserted between the thiophene rings. The thienylenevinylene and thienylenebenzene oligomers **14** and **15** are calculated to be planar. The linking groups are part of the delocalized π-system. Whereas compounds of the last mentioned two series are energetically favored in the *all-anti* conformation the structure of the oligo(thienylenemethines) **13** is less clear. Isomeric structures of the pentamers are presented in Fig. 4. The two *all-syn* structures **B** and **C** of **13** are higher in energy than the *all-anti* structure **A** with 2.1 kcal/mol and 9.1 kcal/mol, respectively, calculated with the 3-21G* basis set and 2.6 kcal/mol and 8.4 kcal/mol, respectively, calculated with the 6-31G* basis set.

The *all-anti*-conformer **C** is the global minimum. Whereas the *all-anti* conformer is planar the *all-syn* conformers are slightly distorted. The torsional angles are less than 15°. The trimer is most stable in the planar *all-syn* configuration. The



	16	**11a** (N=6)
TD -DFT		
B3LYP / 3-21G*	1.98 (1.95)	1.61 (2.67)
B3LYP / 6-31G* [a]	1.93 (1.91)	1.58 (2.61)
ZINDO-CIS	1.69 (2.23)	1.59 (2.97)
Exp. (in CH_2Cl_2)	1.57 [31]	1.24 [27]

[a] TD-DFT calculations based on B3LYP/6-31G* optimum geometries

Fig. 5. The lowest-energy A_g–B_u transitions of the oligothiophene dications **16** and **11a** in eV (*f*-values in parentheses).

Table 3
Calculated absorption wavelengths λ in nm of the oligothiophene dications **11a–11d**

N[c]	Neutral compounds[a]	Parent compounds		Substituted compounds			Hydrocarbon dications[b]
	1 3-21G*	**11a** (R = H) 6-31G*	**11a** (R = H) 3-21G*	**11b** (R = NH_2) 3-21G*	**11c** (R = SH) 3-21G*	**11d** (R = CN) 3-21G*	**12** 3-21G*
4	423 (1.24)	569 (1.44)	566 (1.40)	608 (1.76)	652 (2.02)	619 (1.79)	544 (2.38)
5	469 (1.64)	670 (2.08)	665 (2.10)	716 (2.38)	758 (2.58)	714 (2.45)	627 (3.02)
6	506 (2.02)	775 (2.64)	769 (2.67)	830 (2.91)	868 (3.08)	813 (2.98)	708 (3.64)
7	537 (2.38)	884 (3.13)	878 (3.17)	956 (3.34)	986 (3.49)	9.19 (3.43)	786 (4.20)
8	551 (2.70)	1000 (3.55)	995 (3.58)	1095 (3.62)	1114 (3.81)	1031 (3.81)	862 (4.72)
9	582 (3.07)	1125 (3.88)	1121 (3.90)	1256 (3.75)	1254 (4.03)	1150 (4.12)	937 (5.18)
10	599 (3.41)	1263 (4.12)	1261 (4.12)	1436 (3.75)	1407 (4.16)	1280 (4.35)	1009 (5.57)
11	613 (3.75)	1416 (4.25)	1415 (4.24)	1633 (3.69)	1574 (4.21)	1419 (4.52)	1081 (5.89)
12	625 (4.09)	1581 (4.31)	1582 (4.28)	1845 (3.60)	1750 (4.22)	1571 (4.61)	1149 (6.15)
13	635 (4.43)	1754 (4.33)	1756 (4.30)	2065 (3.52)	1936 (4.21)	1731 (4.66)	1222 (6.32)
14	643 (4.77)	1941 (4.30)	1944 (4.27)	2290 (3.45)	2130 (4.18)	1900 (4.68)	1292 (6.48)[d]
ΔE_∞[e]	1.52	0.09	0.09	<0.01	0.12	0.19	0.48

The oscillator strengths given in parentheses are dimensionless quantities. The bandgaps ΔE_∞ are in eV (TD-DFT B3LYP).

[a] Spectral parameters calculated for planar oligothiophenes.

[b] In this series the number N is defined by units of four methylene groups. The compounds are calculated with structures corresponding to *all-anti* conformations of oligothiophenes.

[c] For λ-values of $N = 15$ to $N = 18$ see Table 2.

[d] For comparison: The corresponding spectral data of the *all-s-trans* polyene (C_{2h}) with 28 double bonds are 1274 nm (f 10.80).

[e] Energy gaps calculated by linear extrapolation of transition energies vs. $1/N$.

all-syn structure of oligo(thienylenemethine) **13B** ($N = 5$) reminds one of the structure **11aB** of the parent dication (cf. Fig. 4). The sulfur atoms are positioned on a concave face of the curved oligomer. The insertion of methine groups makes a bent structure possible with sulfur atoms on a convex surface.

According to the BLA indices compounds of the series **13–15** are essentially quinoid. Like in series **11a**, the quinoid character is weakened with increasing the chain length in favor of the benzenoid one. Extension of the **C**-type structure of **13** and final cylization may lead to new macrocyclic oligomers with sulfur atoms positioned outside. This ring structure is distinctly different from the experimentally known cyclic diactions derived from **B** first synthesized in [58] and the recently studied cyclothiophenes [59]. These ring compounds exhibit inside positioned sulfur atoms.

As shown in Table 4 the absorption wavelengths of oligomers of series **13–15** increase in the sequence **13** < **14** < **15**. The thienylene shift in series **13** is nearly constant but is increasing in the series **14** and **15**. In the last mentioned cases the oligomer dications absorb in the NIR at relatively short chain lengths. Spectral data of members of series **14** are known [39–41]. Alkyl-substituted compounds of the structure **14** with $N = 8$ and $N = 12$ absorb at about 1800 and 2300 nm, respectively [39]. These oligomer dications belong to the most bathochromic metal-free organic NIR dyes with closed shell structures. The calculated absorption wavelengths are again underestimated by TD-DFT. Without taking into account the spectral effects of the substituents in the calculation the deviation between theory and experiment amounts to about 0.3 eV (cf. footnote of Table 3).

Replacing the vinylene groups of **14** by phenylene groups increases greatly the absorption wavelength and the absorption intensity. Without considering the error of theoretical models the absorption wavelengths of **15** may reach 2000 nm region with seven thiophene rings only. Concomitantly, the oscillator strength calculated by TD-DFT increases strongly resulting in an extremely large value of $f = 12.8$.

4.4. The nature of the dicationic chromophores

Since oligothiophene dications are fully planar these compounds constitute a class of ππ*-chromophores. Within the π-approximation the lowest-energy transition of the parent compounds is characterized by an electron transfer from the terminal thiophene rings to the inner thiophene rings. Dicationic as well neutral compounds are characterized by a single intense electronic transition at low energies. However, the

Table 4
Calculated absorption wavelengths λ and oscillator strengths f (in parentheses) of bridged thiophene-based oligomer dications (TD-DFT B3LYP/3-21G*)

N	**13**		**14**[a]		**15**	
	TD-DFT	ZINDO-CIS	TD-DFT	ZINDO-CIS	TD-DFT	ZINDO-CIS
3	493 (0.47)	590 (1.60)	547 (1.80)	594 (2.45)	705 (2.24)	799 (3.19)
5	706 (2.70)	780 (2.75)	812 (4.17)	847 (3.76)	1269 (3.61)	1455 (5.18)
7	887 (4.20)	923 (3.53)	1109 (5.91)	1083 (3.75)	2014 (3.77)	1905 (12.84)
9	1068 (5.56)	1044 (4.25)	1465 (6.95)	1349 (5.45)	–	–
11	1236 (6.84)	1133 (4.98)	1945 (6.99)	1705 (5.76)	–	–

[a] $N = 8$: Becke3LYP/3-21G* 1277 nm (0.97 eV), PB0/3.21G* 1271 nm (0.98 eV), Exp. 1823 nm (0.68 eV) [39].

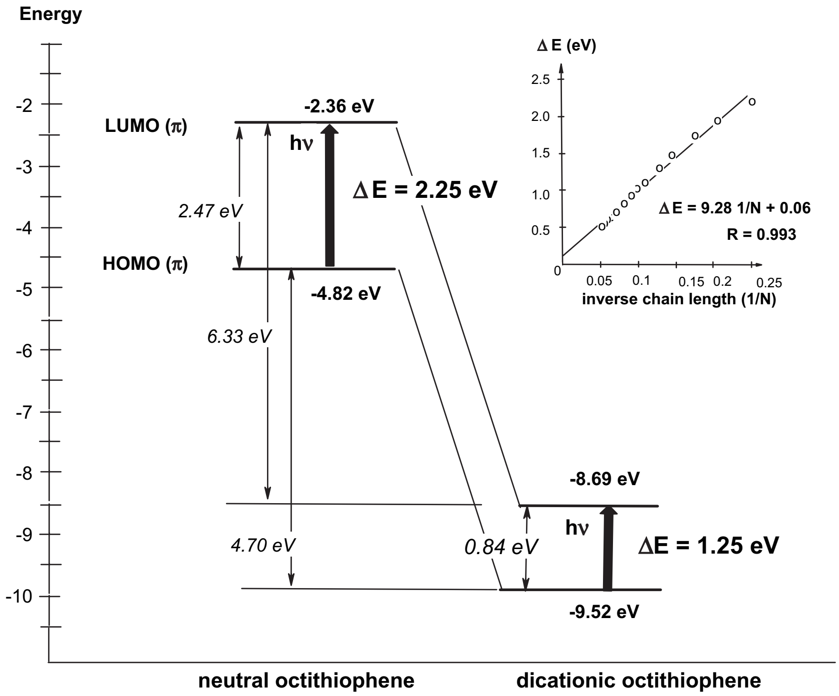


Fig. 6. Frontier orbitals (Kohn–Sham MO energies) of the neutral and doubly oxidized oligo thiophenes with eight thiophene rings, energy gaps between frontier orbitals and energy differences between the HOMOs und LUMOs (values in italics). Inserted in the box: plot of the calculated transition energies of the dications **11a** against the inverse number of thiophene rings and the linear correlation.

transitions differ greatly in the absorption wavelengths and in the intensities. Dications absorb more intensely at much longer wavelengths.

Inspection of the Kohn–Sham MO energies gives a simple explanation of the strong bathochromism of dications relative to neutral compounds. As exemplified with octihiophenes (**11a**, $N = 8$) in Fig. 6 the excitation energy of the dication is about 1 eV lower than the energy of the neutral compound. Both the HOMO and the LUMO of the dication are significantly lowered in energy but the LUMO to a much larger extent. The LUMO of the dication is more stabilized relative to the HOMO by 1.63 eV relative to the corresponding neutral compound. Qualitatively, the energetic characteristics do not alter if another chain length is considered. However, the relative size of the energy gap of the LUMO increases from 1.63 with $N = 8$ to 2.02 eV with $N = 18$.

If all 15 calculated vertical transition energies of the parent dications of Table 2 are considered the linear extrapolation in inverse numbers N of thiophene rings ($1/N$) results in an intercept on the ΔE axis of 0.09 eV (cf. Fig. 6). Because of a slight curvature of the correlation a reduced choice of the data will affect the calculated intercept. Thus linear extrapolation of data with only lower-size oligomers and of data of only larger size oligomers results a more positive and in negative intercepts, respectively.

Experimental spectral data for extrapolation are available in two series of compounds. The bandgap calculated from the excitation energies of four doubly oxidized poly(α,α-silylpolyalkyl)thiophenes ($N = 5–8$), measured in an electrolyte solution [35], resulted in 0.08 eV. On the other hand, extrapolation of the three lowest-transition energies of the parent oligthiophene dications **11a** ($N = 4$, 8 and 9) measured in zeolite [29] led to a bandgap of 0.09 eV. In view of the small number of experimental data in each series the excellent agreement between theory (0.09 eV) and experiment (0.08–0.09 eV) should not be overestimated.

The discussion about the chromophore of the dication presupposes that the oligomer actually exists in a closed shell symmetric structure in the ground state. Both S/S- and S/T-instability may cause changes in structure and properties and has therefore to be considered. To probe the inclination for symmetry breaking calculations were performed with the BH and HLYP functional. A higher contribution of HF exchange of the functional allows a more realistic description of the bond characteristics than B3LYP [3]. In contrast to monocationic polymethine dyes, however, no indication for symmetry breaking of oligothiophene dications was found. However, in agreement with earlier reports [10,11] larger size oligothiophene dications are S/T-unstable. The S/T-instability indicates the presence of a biradicaloid NIR chromophor [47]. The S/T-instability is consistent with the fact that the S/T splitting energies are low for large size oligothiophene dications.

After mixing the frontier orbitals to destroy α,β-spatial symmetry in the initial guess, solutions of a spin-broken symmetry may be obtained. Sexithiophene is the first member of series **11a** where a broken symmetry is detectable [11,13]. Thus $N = 6$ marks the cross point in the calculation with the 6-31G* basis set. The cross point is the same with the 3-21G*. The open shell calculation (UDFT) in that case results in a lowering of the energy relative to the energy of the conventional closed shell structures. Whereas the stabilization energy of the sexithiophene amounts only to 0.1 kcal/mol the energy increases to 4.7 kcal/mol with the ring size of $N = 18$ (3-21G*). Larger stabilization energies are calculated with the more extended basis sets [11,12].

The lower-energy spin-contaminated structure of UDFT calculations is indicated by $\langle S^2 \rangle$ values. The term $\langle S^2 \rangle$ stands for the expectation values of the spin square operator ($\langle S^2 \rangle$). Although the absolute value is not correctly defined at the UDFT level it represents a useful probe for the occurrence of spin-contaminated states of lower-energy. The $\langle S^2 \rangle$ value is zero for a singlet state and is larger than zero for a spin-contaminated state. In the following some $\langle S^2 \rangle$ values without spin projection are given in parentheses. Apart from the parent dications of the series **11a** (e.g. $N = 6$ (0.18), $N = 8$ (0.72), $N = 12$ (0.96), $N > 15$ (1.00)) singlet/triplet instabilities are encountered with the bridged dications **14** with $N = 9$ (0.97) and **15** with $N = 3$ (0.33) and higher members of these series. The resulting structures possess biradical character and were discussed in term of the two-polaron pairs. This behaviour is not restricted to dicationic oligomers. Neutral quinoid compounds may also be S/T-unstable. UDFT calculations of the class-2 compounds **5a** (0.70), **5b** (0.11) and **5c** (0.81) as well as **6** (1.02) led to spin-contaminated states lower in energy than by RDFT calculations. Interestingly, paramagnetic species were detected by ESR spectroscopy in the cation salts of substituted tetramer and hexamer dications of the series **11a** [31] and of **5c** in solution [23,24]. The results have been discussed in terms of biradical [23,24] and two-polaron structures [31]. In this connection it is worth mentioning that the triplet state is situated only slightly above the spin-contaminated singlet state.

Examining the spin-restricted and spin-unrestricted solutions of **11a**, $N = 6$, Gao et al. [10] found notable differences in the UV–Vis–NIR transition energies of spin-restricted closed shell and spin-unrestricted open shell calculations. In the case of larger size dications we found small differences in the energy of the intense lowest-energy transitions. The differences amount at best to 0.06 eV for $N = 12$, 14 and $N = 16$ and to less than 0.01 eV for $N = 18$. Similar results were obtained for derivatives of **11a** such as the dicationic **14** ($N = 9$ and $N = 11$), and for the S/T-unstable neutral oligomers (e.g. $N = 4$). In the case of the open shell calculations, however, forbidden transitions appear in addition to the intense ones. Inspection of the frontier orbitals confirms that the lowest-energy transitions of closed and open shell systems are related. As depicted in Fig. 7 with the transitions of **11a** ($N = 8$) the electronic transition in the closed shell case occurs mainly between the doubly occupied HOMO and the LUMO and in the open shell case between degenerate singly occupied orbitals (SOMOs) and degenerate empty orbitals. As a consequence the allowed transitions in the latter case are accompanied by a forbidden one. The numerical agreement between the energies of the allowed lowest-energy transitions of the closed and open shell calculation (0.45 eV) is fortuitous. The intensity of the lowest-energy transition calculated by open shell BS-UDFT is considerably lower than by RDFT.

Since the low-lying LUMOs of dications and of the acceptor-substituted neutral compounds are obviously responsible for the long wavelengths absorption the candidates for NIR chromophores should not restricted to sulfur-containing oligomers. NIR chromophores may likewise be encountered in other series of dications. The doubly oxidized tetraphenyl phenylenediamine **16** may serve as an example. Like sulfur in the thiophene-based oligomers external donor amino groups of **16** may contribute to the stabilization of the dication (Fig. 8).

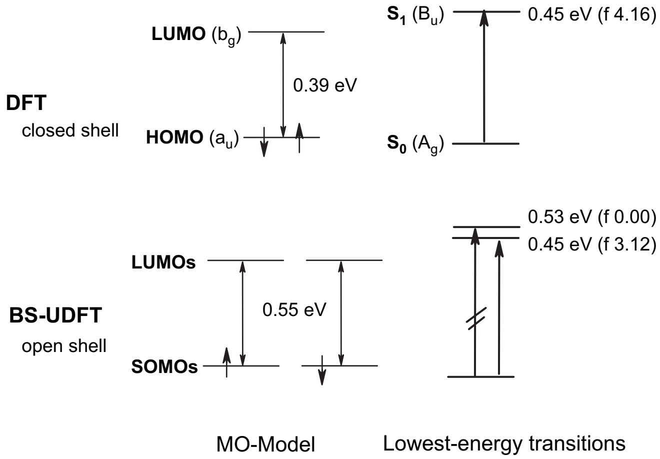
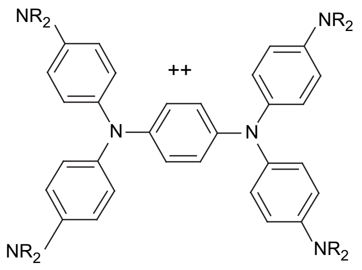


Fig. 7. Lowest-energy electron transitions of octithiophene dication in terms of MOs and term levels calculated by closed and open shell TD-DFT.

5. Conclusions

The color of thiophene-based oligomer ions generated by oxidation of neutral compounds has several quite different origins. Cation radicals, dimerized cation radicals, dications and compounds in higher oxidation states may be formed. The comparably stable dications absorb very intensely at long wavelength. The maximum absorption wavelengths hitherto measured for dications with about 2200 nm exceeds the maximum absorptions wavelength of cyanine dyes by more than 500 nm. According to TD-DFT calculations of oligothiophene dications absorption wavelengths of nearly 3000 nm (0.45 eV) may be reached with about 18 thiophene rings in the chain. The calculated intensity of the absorption is extremely large. Linear extrapolation to infinite chain lengths resulted in a band gap of 0.09 eV. Oligothiophene dications are candidates of low-gap polymers. The large absorption wavelengths



16

R=Me:	TD-DFT	939 nm	1.32 eV (f 1.09)
	ZINDO-CIS	1052 nm	1.18 eV (f 1.40)
	Exp.	1090 nm	1.13 eV (lgε 4.96) [60]

Fig. 8. A nitrogen containing dication absorbing in the NIR [60].

of dications are due to the fact that the energy of the LUMO lowered more than the energy of the HOMO. This interpretation also holds for the neutral oligomers when substituted by acceptor groups. At sufficiently long chain length these compounds are also candidates for NIR chromophores.

The parent oligothiophene dications and derivatives and thiophene bridged oligomers were calculated by spin-restricted DFT (RDFT). These dications correspond to bipolarons. At longer chain lengths spin-unresticated DFT (UDFT) calculations result in energetically slightly favored open shell structures (two-polarons). Calculation of spectral absorptions of large size parent compounds revealed, however, that the lowest-energy of the first intense transition is nearly the same in closed and open shell calculation.

Thiophene-based oligomer dications are well characterized by the calculated CC-bond length alteration of the rings, the bond lengths between the rings and the isotropic nucleus-independent chemical shifts of the individual rings. Conclusions reached by the different indices are consistent. In general, the bonding in the dications is more thienoquinoid than thienoaromatic. There are, however, changes towards more aromatic rings dependent on the position of the ring in the chain and with the chain length.

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